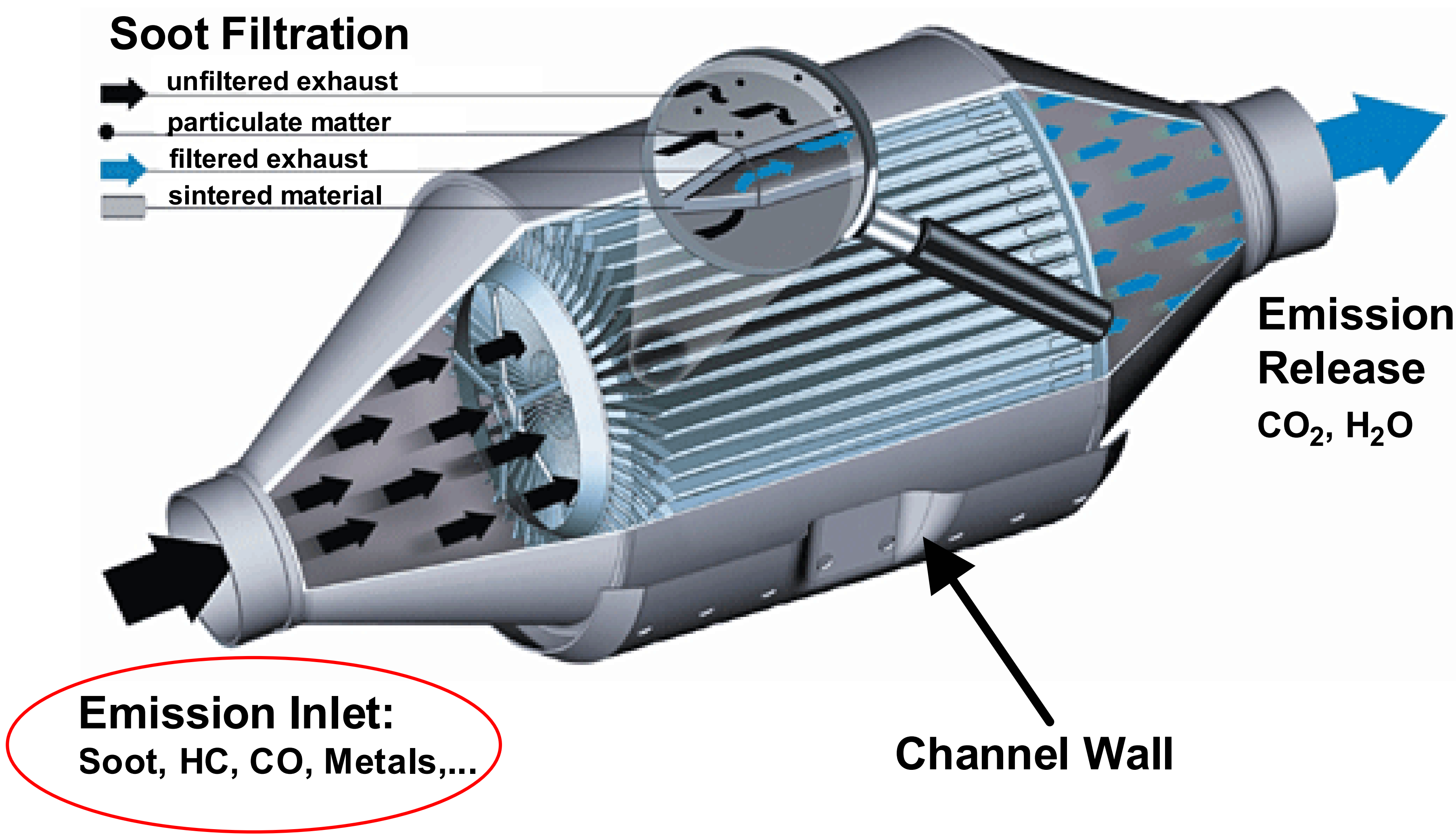
Materials Science & Technology

Penetration of nano-sized metallic fuel additives from diesel vehicles

A. Ulrich, *A. Wichser, N.V. Heeb,*
T. Mosimann, M. Kasper,
J. Czerwinski,
A. Mayer

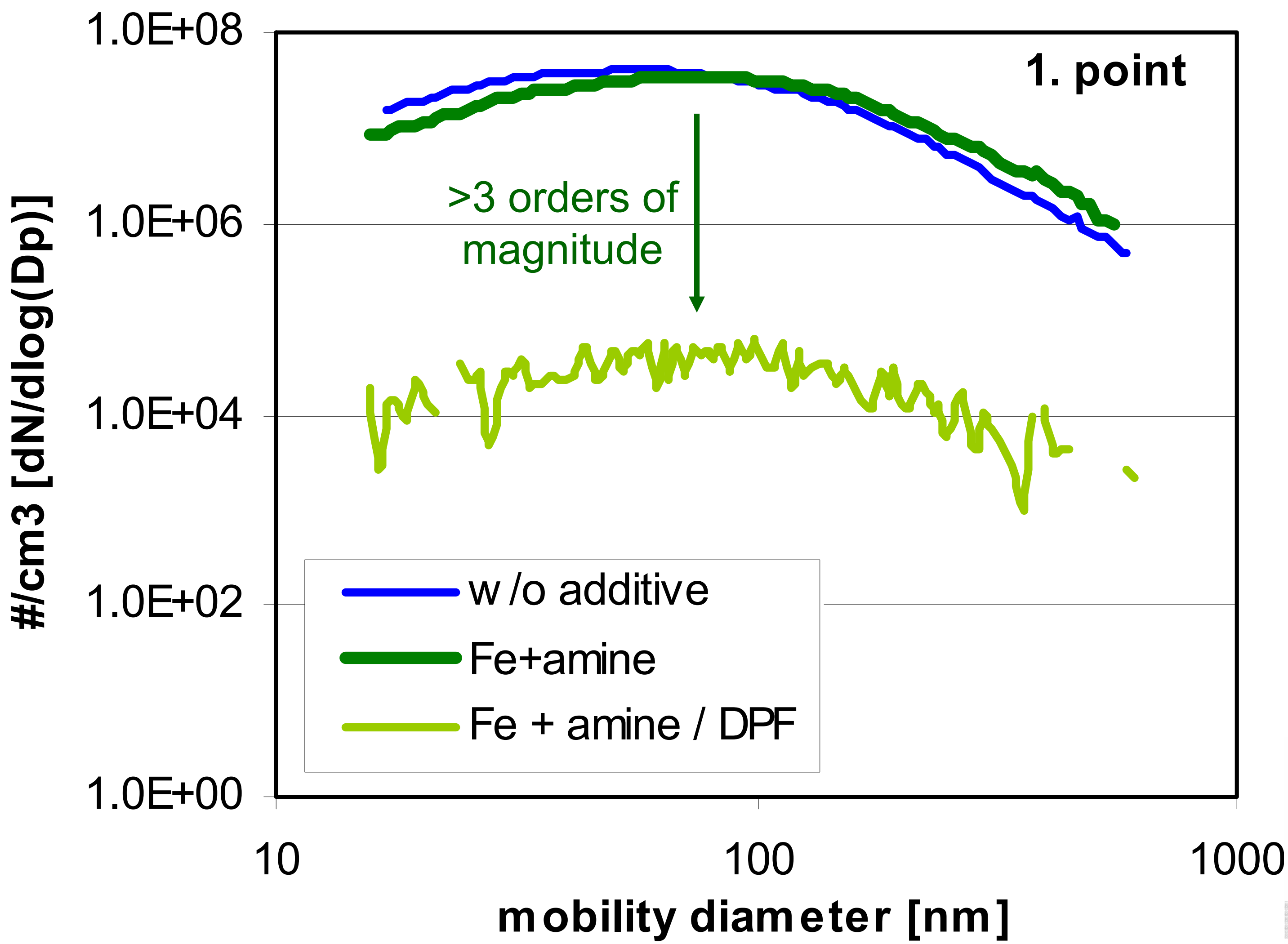
EMPA
Matter Engineering AG
University of Applied Sciences Biel-Bienne, Switzerland
IC Engines and Exhaust Gas Control
TTM Technik Thermische Maschinen

Principle of a Particle Filter Systems (DPF)



Effective reduction of particulates with DPF

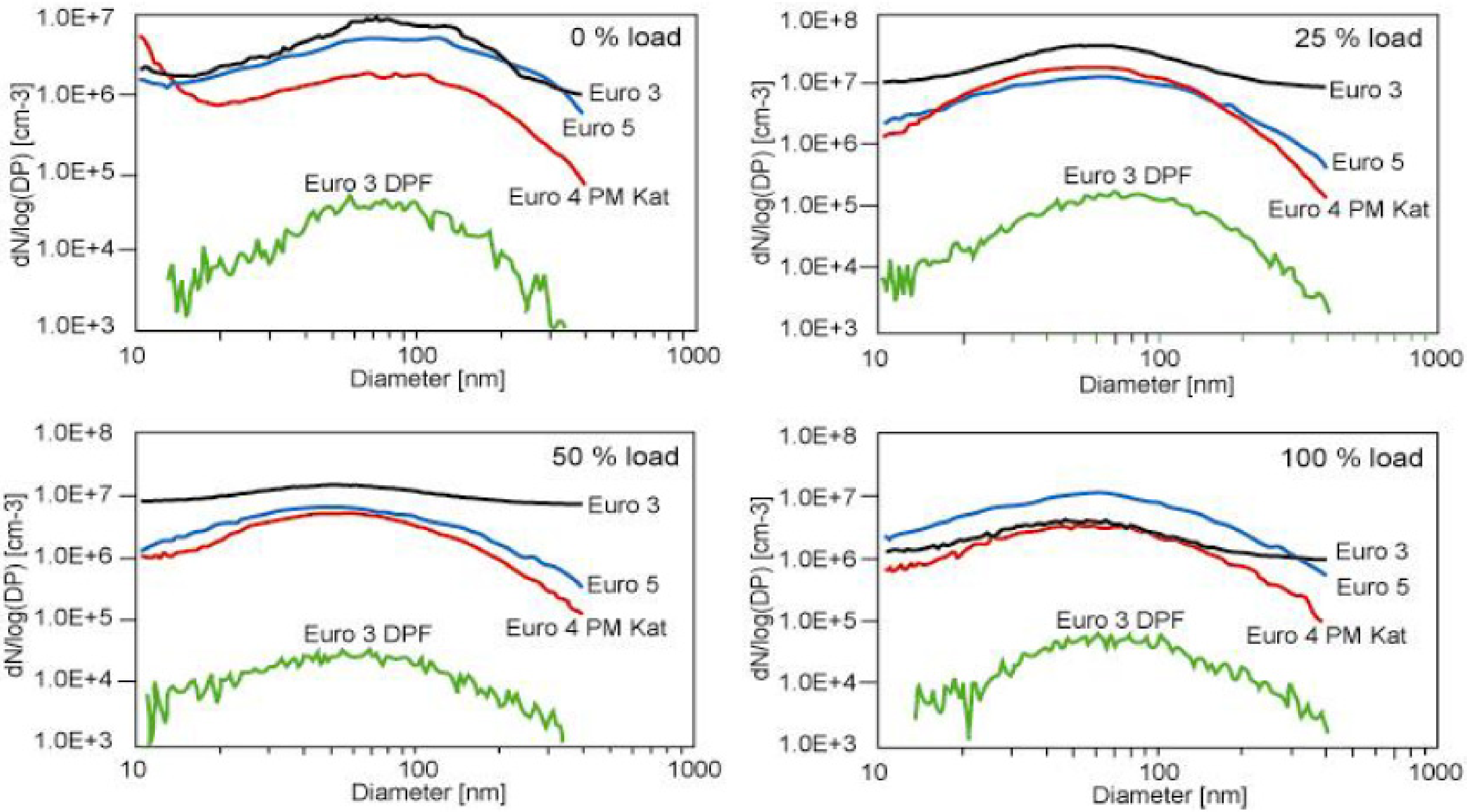
Filtration effectivity >99 %



High potential of diesel particle filters

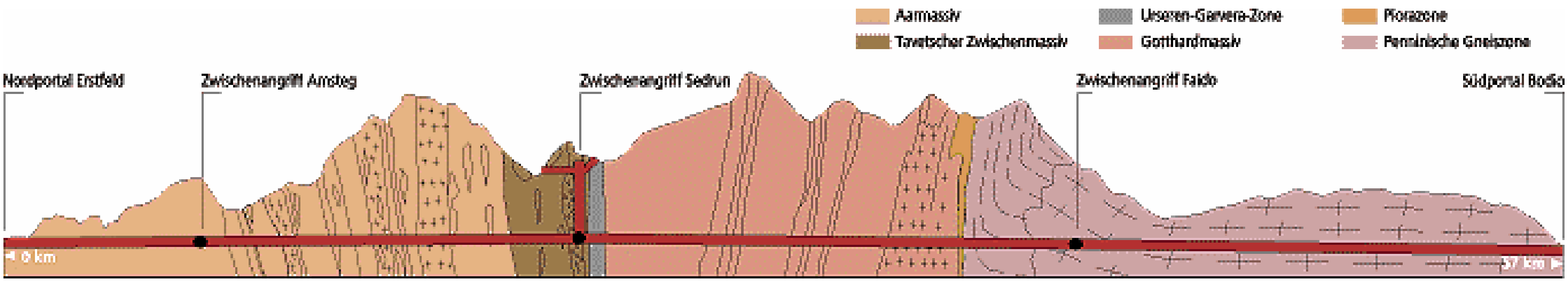
Euro 3 + DPF versus Euro 4 and Euro 5

Poster 38



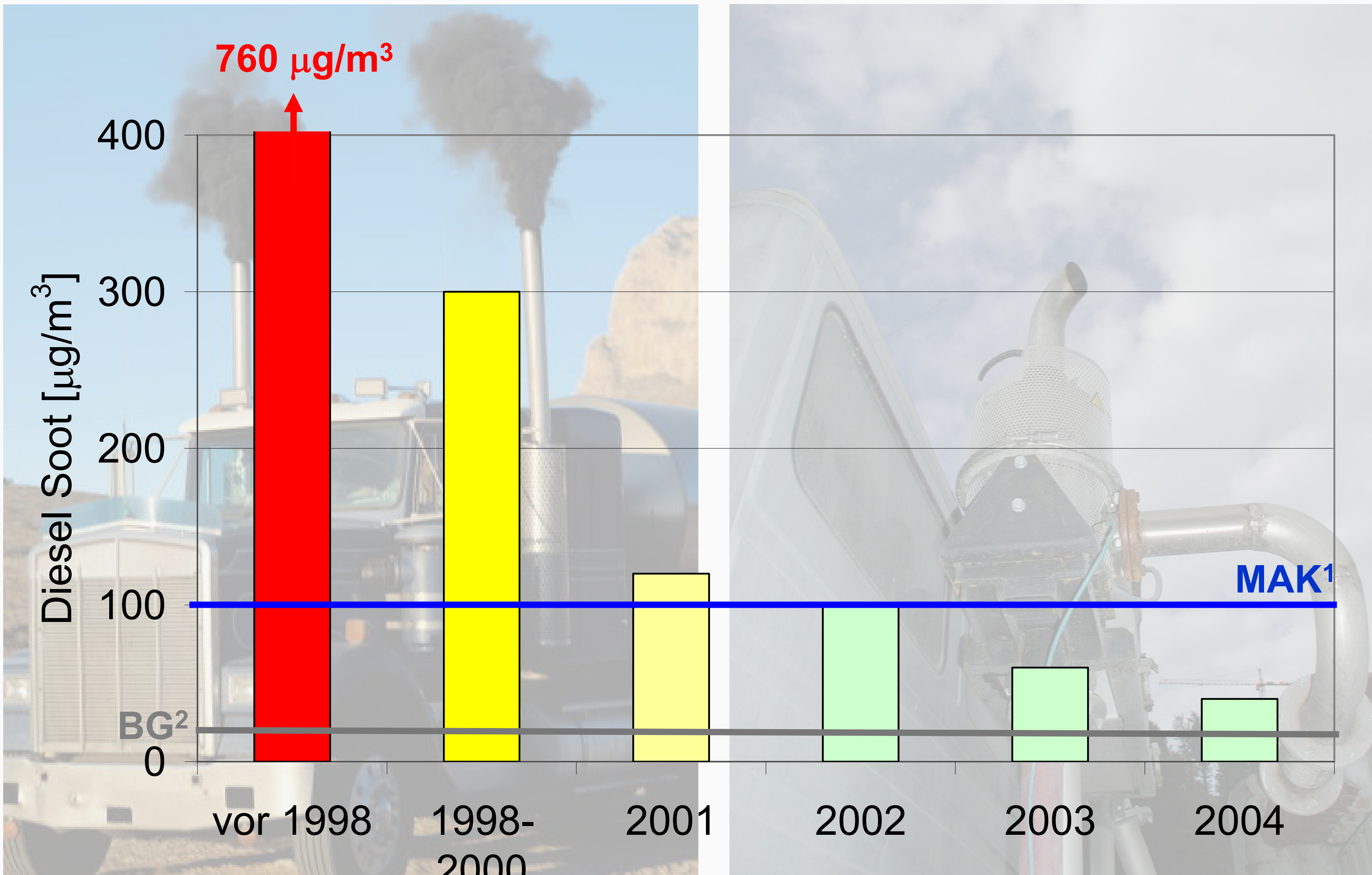
A.Mayer *et al.*, Nanopartikel-Emissionen von HDV Euro 4 und Euro 5 Dieselmotoren im Vergleich zu Euro 3 mit/ohne Partikelfilter, 4.FAD-Konferenz „Herausforderung Abgasnachhandlung für Dieselmotoren“ Dresden 9.11.2006

Alptransit NEAT tunnel (57 km) - the longest rail way tunnel of the world



Soot Reduction at tunnel construction sites due to diesel particle filters (DPF)

SUVA 2004



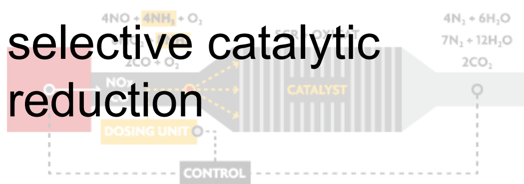
[2] Background concentration

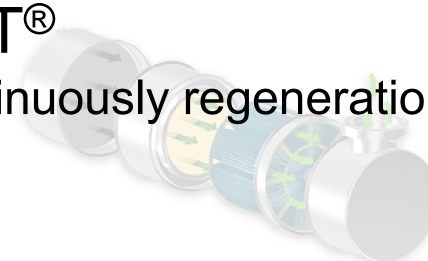
[1] Maximum working place concentration

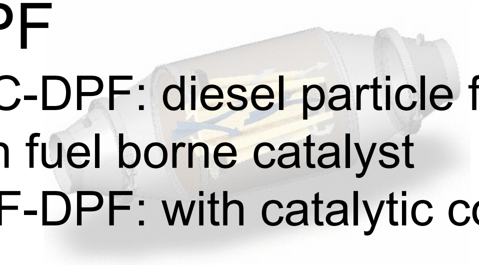
Overview DPF Systems

with Online Regeneration

	NO_x	PM
Continuous	SCR selective catalytic reduction	CRT® Continuously regeneration trap
Discontinuous	NCA NO_x catalytic adsorption	DPF FBC-DPF: diesel particle filter with fuel borne catalyst CSF-DPF: with catalytic coating

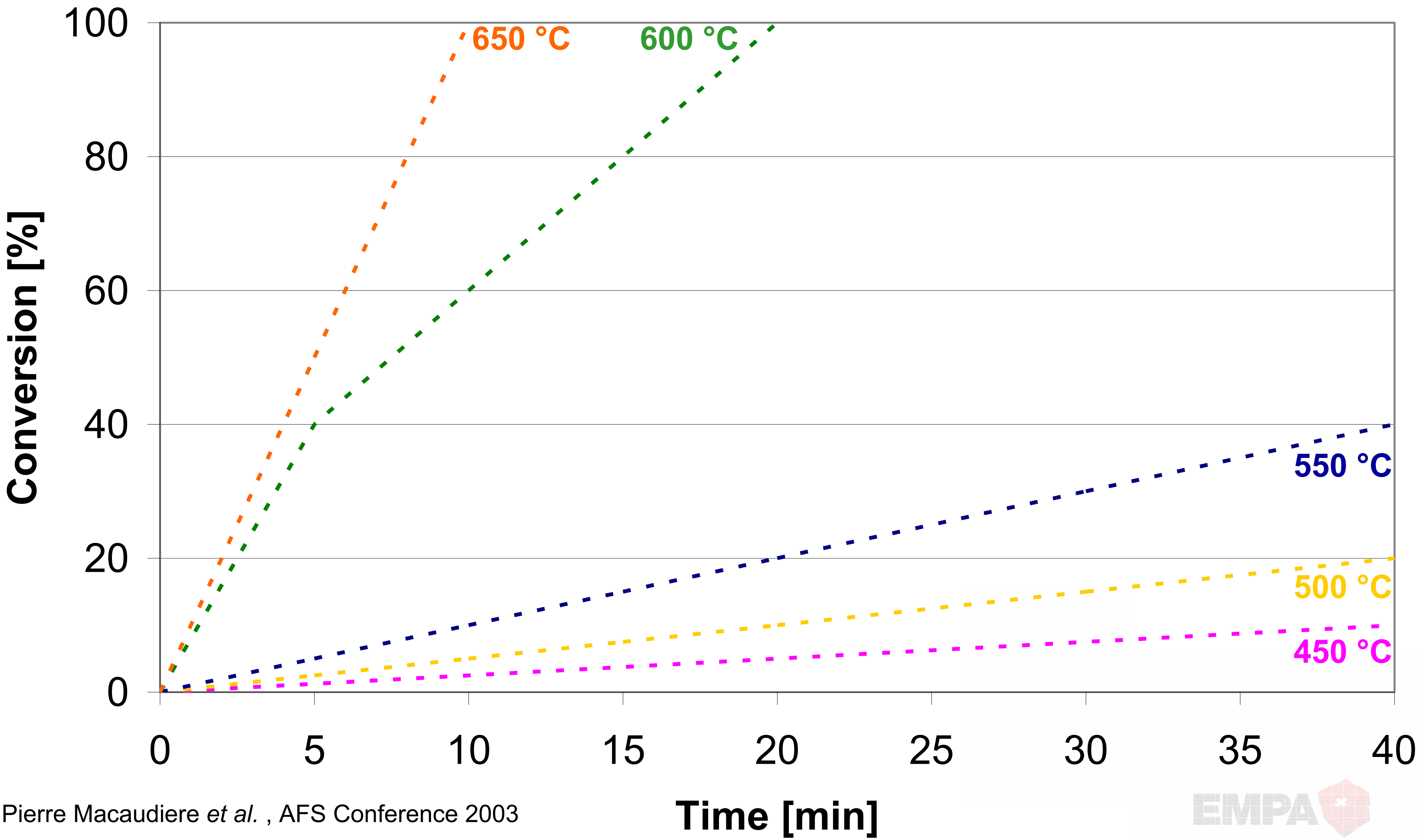






Soot combustion dependent on temperature

···· dotted lines w/o catalytic support (additive)[1]

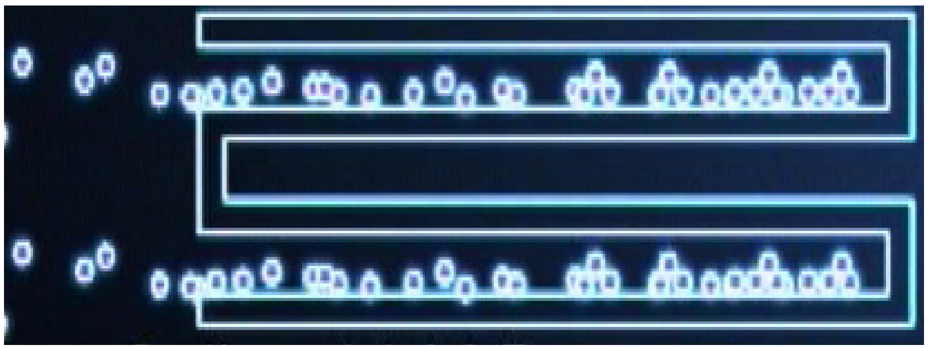


[1]Pierre Macaudiere *et al.* , AFS Conference 2003

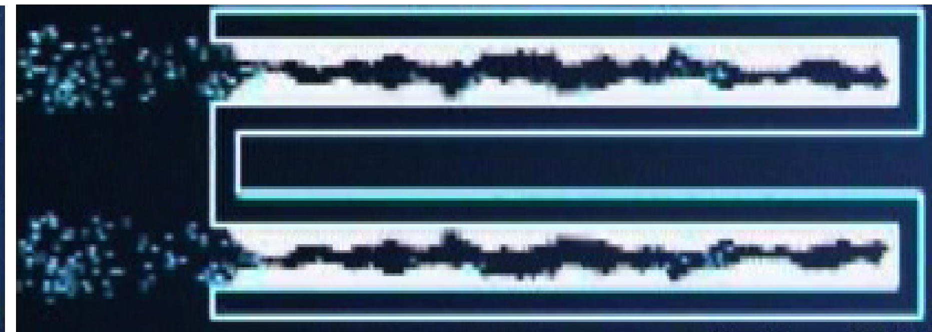
Particle Filter System Concepts

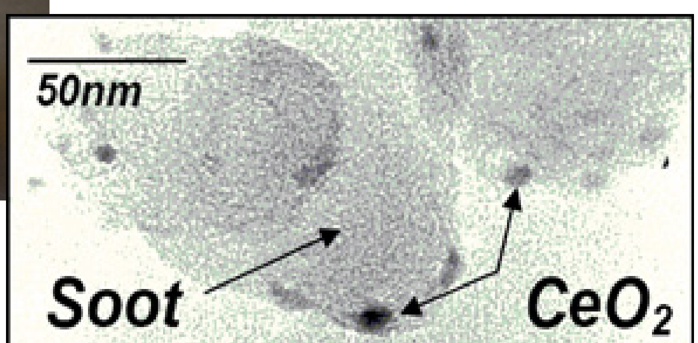
Metal catalyzed combustion of collected soot

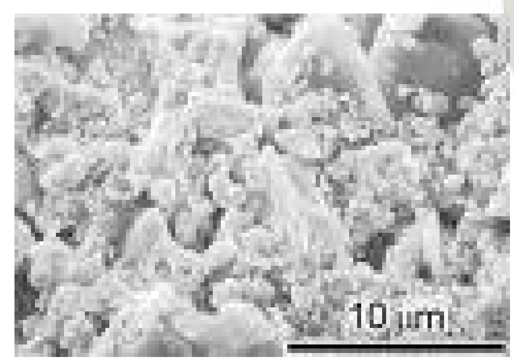
Fuel **b**orne **c**atalyst



Catalytic **c**oating







Particle Filter System Concepts

Metal catalyzed combustion of collected soot

Fuel borne catalyst	Catalytic coating
Addition of metal catalyst to fuel => dosing concept / optimization	**No additional metal in fuel**
Catalyst in soot => catalyst in center of particulates => higher efficiency of regeneration	**Surface catalyst in coating** => direct contact necessary => risk of incomplete regeneration
Shorter regeneration time 4 min for 30g of soot (*G. Belot 2003*)	**Longer regeneration time** 20 min for 30g of soot (*G. Belot 2003*)
Always fresh catalyst	**Possible aging of the catalyst**
Hazard of penetration additive metals, nanoparticles => Increase during regeneration? DPF aging (cracks, ...)?	**Hazard of abrasion lower** than penetration (new DPF) => aging?
Hazard of precipitation / deposit (homogeneous mixture / mass balance)	**Hazard of accumulation** => **release; poisoning** e.g. sulphur at Pt surfaces

Precipitation of a Fuel Additive

Example for a Mass balance for Cerium - Total mass per cycle

	Cerium
Additive quantity	473 mg
Total mass ELPI without trap Total mass ELPI with trap	2.05 µg 0.037 µg
Total mass exhaust gas with trap Total mass exhaust gas with trap	15.37 mg 0.27 mg
Deposition in engine, tank, etc. Deposition in trap Ermitted into ambient	457 mg 15.1 mg 0.27 mg
Filtration rate in engine Filtration rate in trap **Total filtration rate system**	96.7 % 98.2 % **99.94 %**
Emissions factor	0.96 µg/kWh 0.2 µg/Nm³

A. Ulrich *et al.*, Anal. Bioanal. Chem. 2003

Release of stored sulphur from Pt coated DPF at T > 400 °C

=> long term operation at low load conditions (VERT 2000 h operation test, S < 50 ppm)
=> PM filtration rate: particle No. >98 %, but bad particle mass
=> Release time > 30 min

Sample ID	Set point	n / M	Δm	t_5	t_6	Amout of water loss	Cl	NO2	NO3	PO4	SO4
		[min^{-1} / Nm]	[mg]	[°C]	[°C]		mg/filter				
LOD							0.03	0.03	0.03	0.03	0.03
V21	2	1400/605	32.1	491	417	11.2	<DL	<DL	<DL	<DL	6.0
V22	2	1400/605	30.3	491	417	10.1	<DL	<DL	<DL	<DL	5.2
V23	6	1400/297	0.2	321	289	0	0.03	<DL	0.08	<DL	0.03
V24	6	1400/297	0.4	321	289	0	0.03	<DL	0.05	<DL	0.2
V25	5	2000/252	0.2	334	309	0	0.05	<DL	0.11	<DL	0.05
V26	5	2000/252	0.4	334	309	0	<DL	<DL	0.03	<DL	0.25
V28	1	2000/530	5.4	481	430	0.8	<DL	<DL	<DL	<DL	1.9
V29	1	2000/530	6.1	481	430	0.9	<DL	<DL	<DL	<DL	2.2
V27	2 (Rep)	1400/600	19.9	501	418	5.9	<DL	<DL	<DL	<DL	4.9
V30	2 (Rep)	1400/600	18.4	501	418	5.3	<DL	<DL	<DL	<DL	4.1

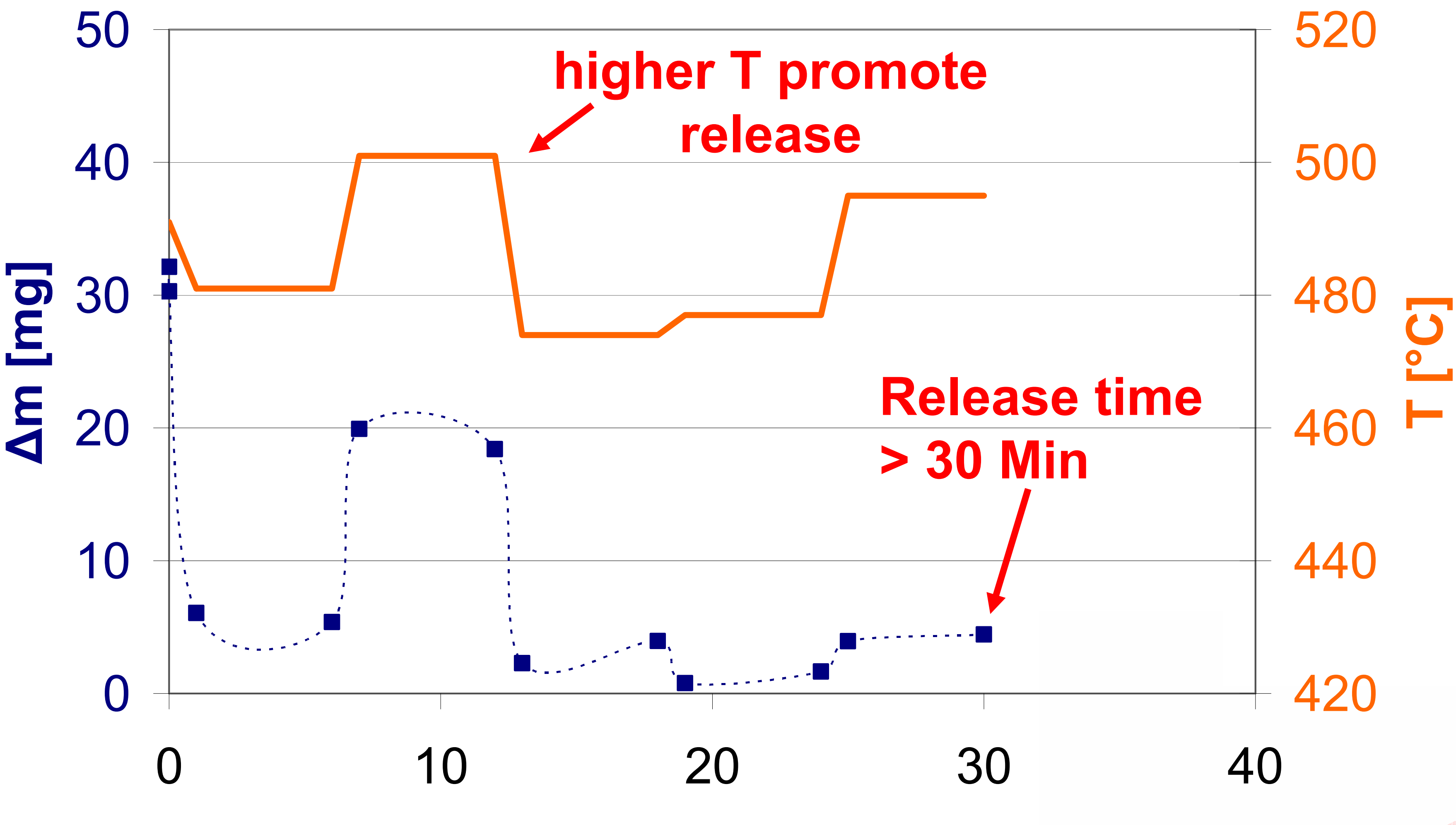
Condensation

Sulphur Artefacts

A. Ulrich *et al.*, 11. ETH Conference on Combustion Generated Nanoparticles 2007
A. Mayer, A. Ulrich *et* al., SAE 2008-01-0332

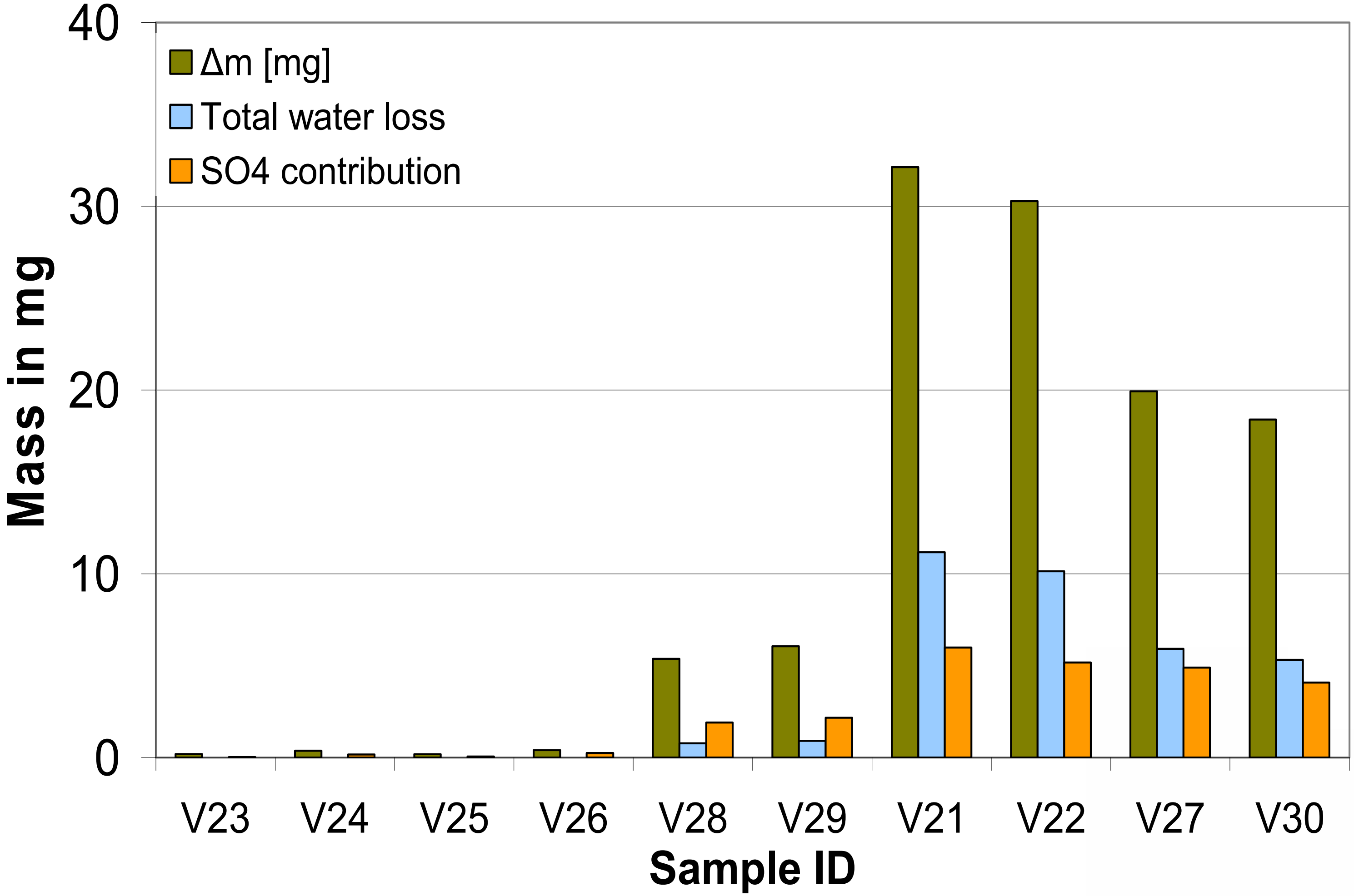
Release time for stored SOx artefacts

Results for DPF 7



A. Ulrich *et al.*, 11. ETH Conference on Combustion Generated Nanoparticles 2007
A. Mayer, A. Ulrich *et* al., SAE 2008-01-0332

Release of stored sulphur from Pt coated DPF at high Temperature long term accumulation at low load condiitons



A. Ulrich *et al.*, 11. ETH Conference on Combustion Generated Nanoparticles 2007
A. Mayer, A. Ulrich *et* al., SAE 2008-01-0332

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Metal catalyzed combustion of collected soot

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  4 min for 30g of soot (*G. Belot 2003*)
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- **Hazard of precipitation / deposit**
  (homogeneous mixture / mass balance)

Catalytic coating

- **No additional metal in fuel**
- **Surface catalyst in coating**
  => direct contact necessary
  => risk of incomplete regeneration
- **Longer regeneration time**
  20 min for 30g of soot (*G. Belot 2003*)
- **Possible aging of the catalyst**
- **Hazard of abrasion lower than penetration** (new DPF) => aging?
- **Hazard of accumulation** => **release; poisoning** e.g. sulphur at Pt surfaces

VERT Procedures

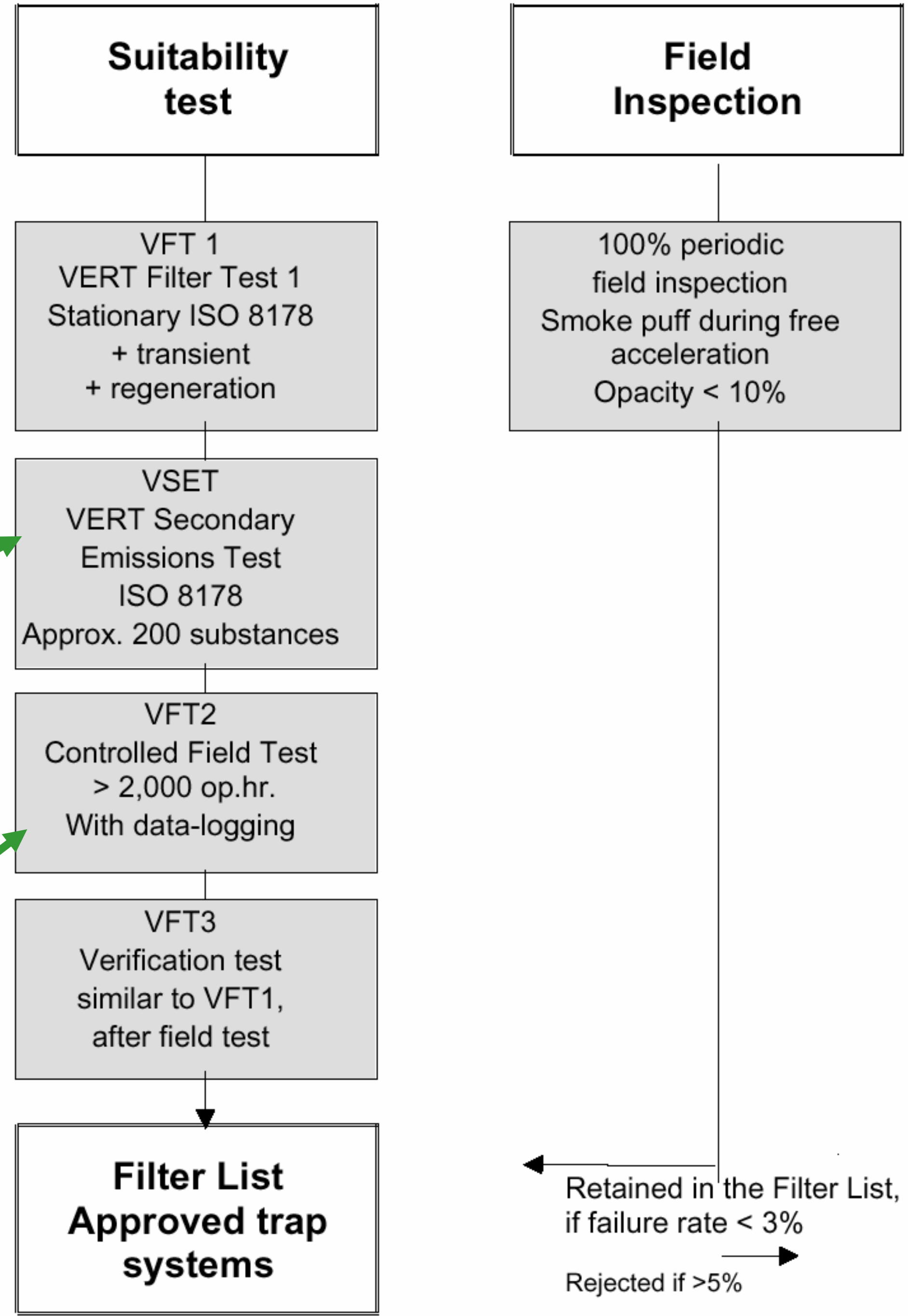
Swiss **N**ational **S**tandard

SNR 277205

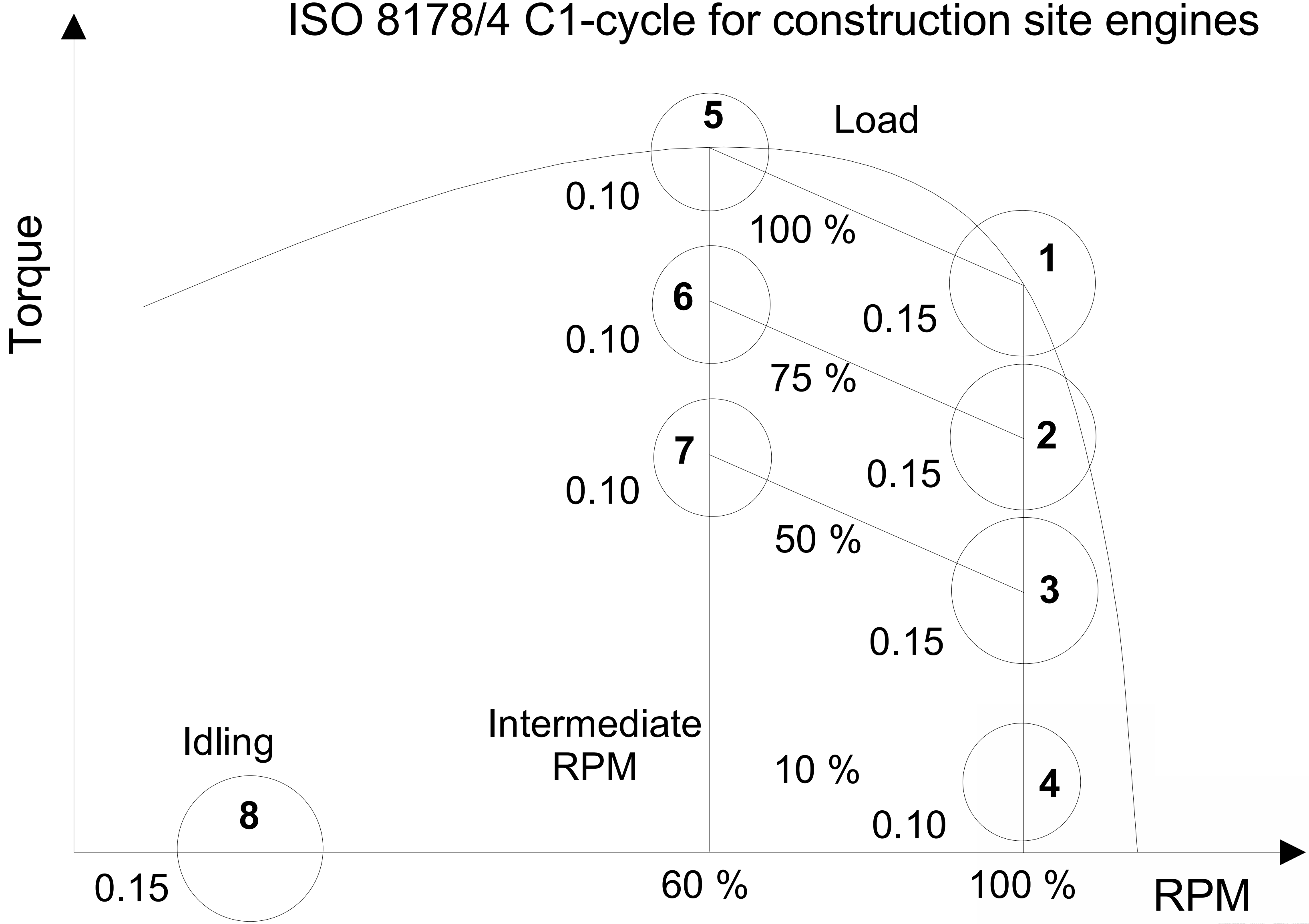
VSET: Possible formation of

- toxic secondary emissions
- penetration of FBC metals
- abrasion of metallic coating

VFT2: long term behaviour



ISO 8178/4 C1-cycle for construction site engines

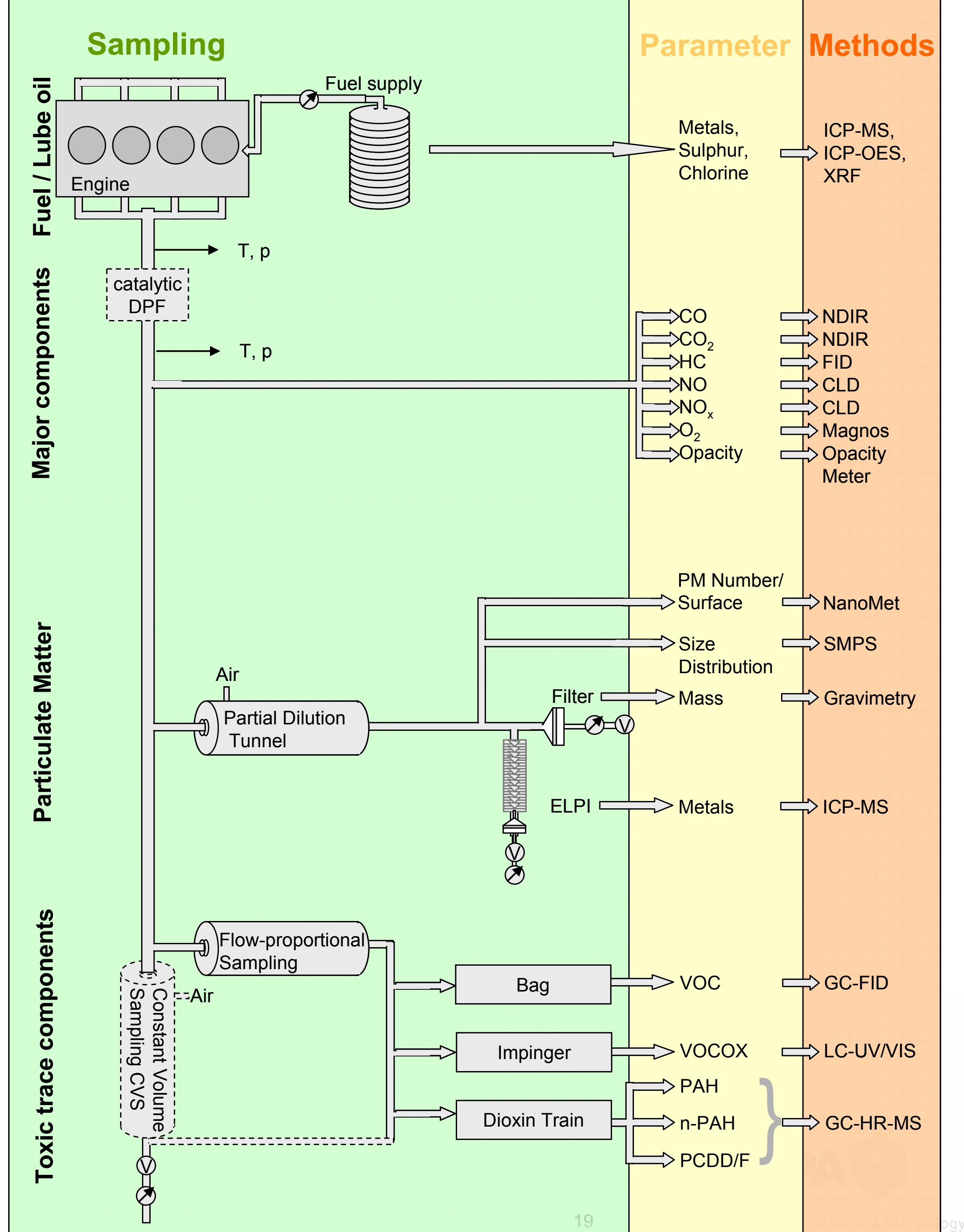


N. Heeb, EMPA Report 167985

VERT Sampling Procedures

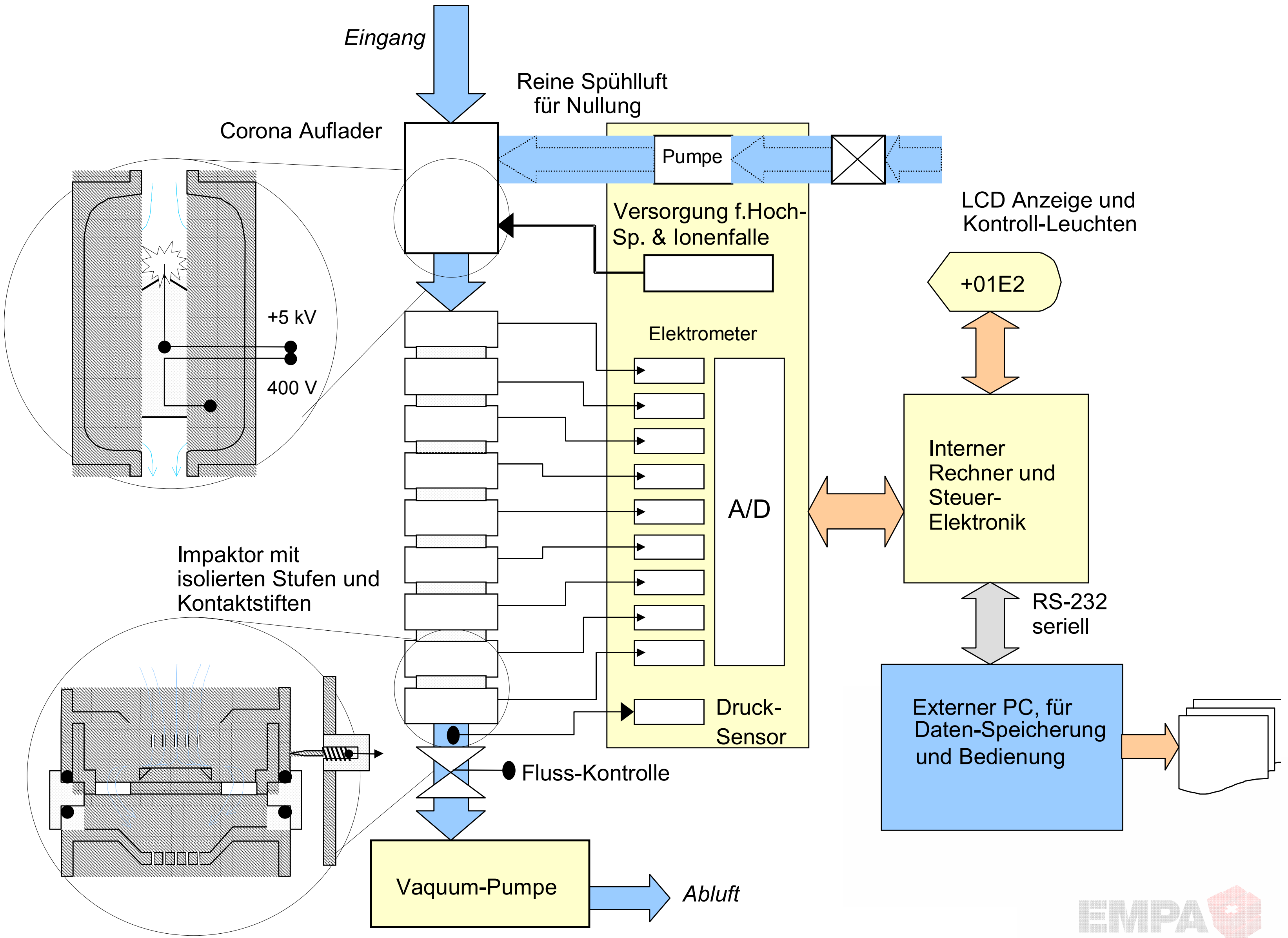
Swiss **N**ational **S**tandard

SNR 277205



Principle of Electrical Low Pressure Impactor

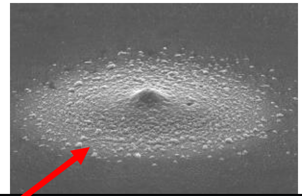
ELPI



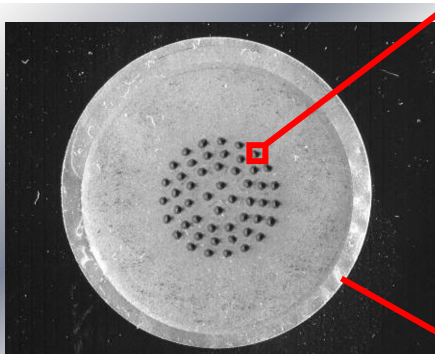
Specification of ELPI impactor

Stage	Dso% [µm]	Di [µm]	Number min [1/cm3]	Mass min [µg/m3]	Mass max [mg/m3]
13	10				
12	6.8	8.4	8.00E+03	22	2100
11	4.4	5.3	2.00E+04	12	1200
10	2.5	3.2	4.00E+04	6.3	630
9	1.6	2	8.00E+04	3.5	350
8	1	1.3	2.00E+05	2	200
7	0.65	0.81	3.00E+05	1	90
6	0.4	0.51	5.00E+05	0.4	40
5	0.26	0.33	9.00E+05	0.17	17
4	0.17	0.21	2.00E+06	0.078	7.8
3	0.108	0.15	3.00E+06	0.035	3.5
2	0.06	0.081	5.00E+06	0.015	1.5
1	0.03	0.042	9.00E+06	0.005	0.5

Analysis
Filter Samples



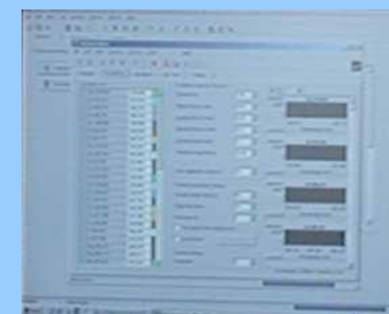
SEM/EDX



eg. ELPI Filter

Sample Digestion Using Microwave

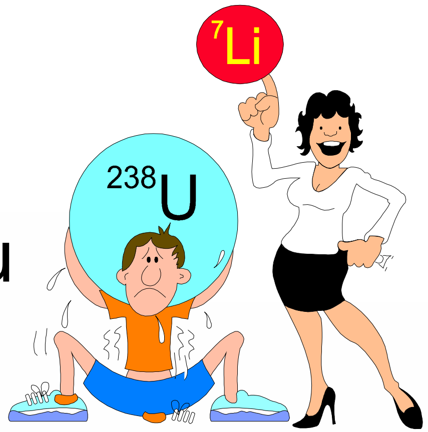
ICP-OES



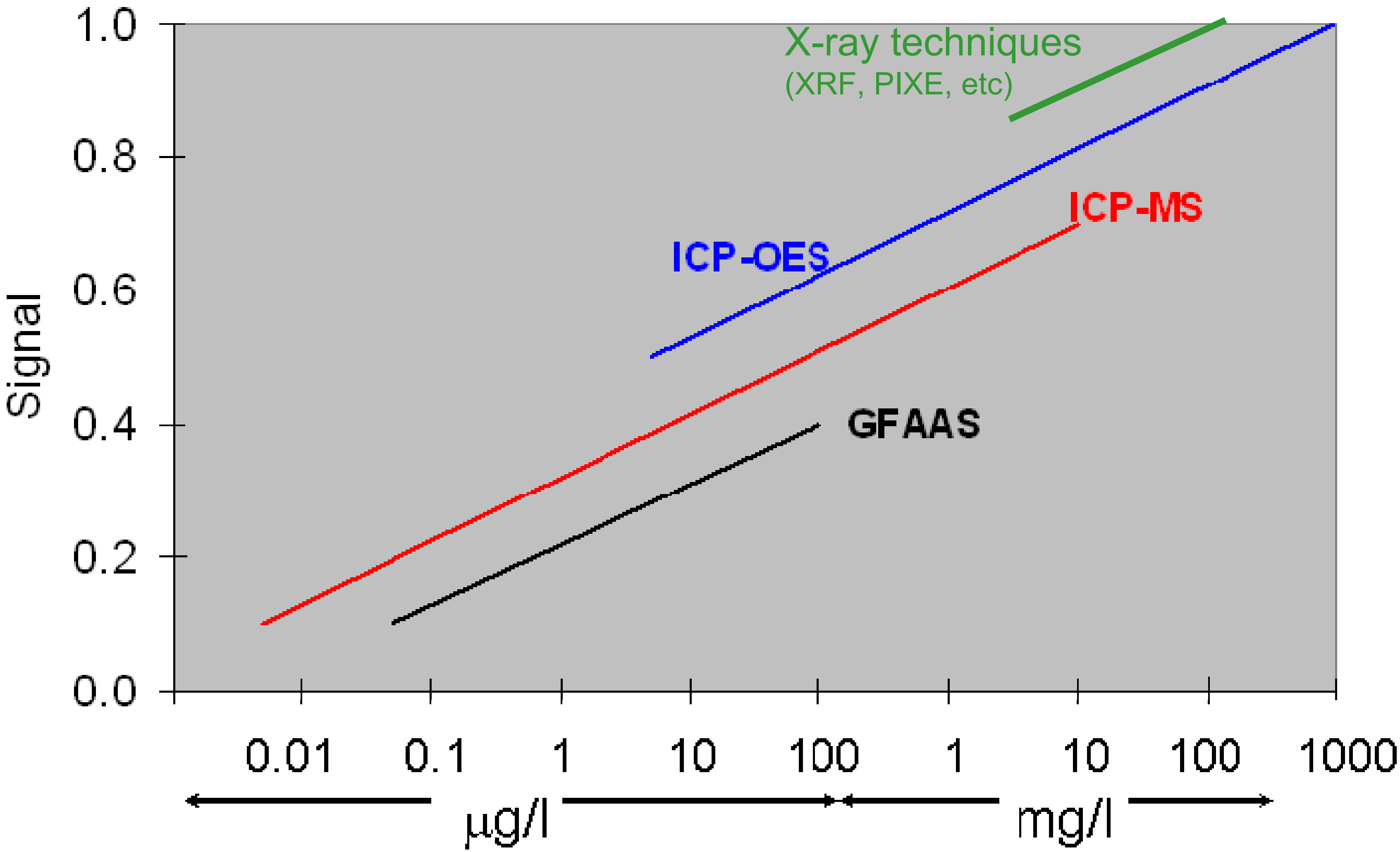
ICP-MS

Characteristics of Plasma Mass Spectrometry ICP-MS

- Fast mulitelement technique 75 elements in 2 min.
- High sensitivity ppb to ppt levels (µg/L - ng/L)
- Large dynamic working range
- Fast scan => transient signals
- Resolution
  quadrupol-ICP-MS ~ 0.7 amu
  high resolution ICP-MS ~ 0. 001 amu

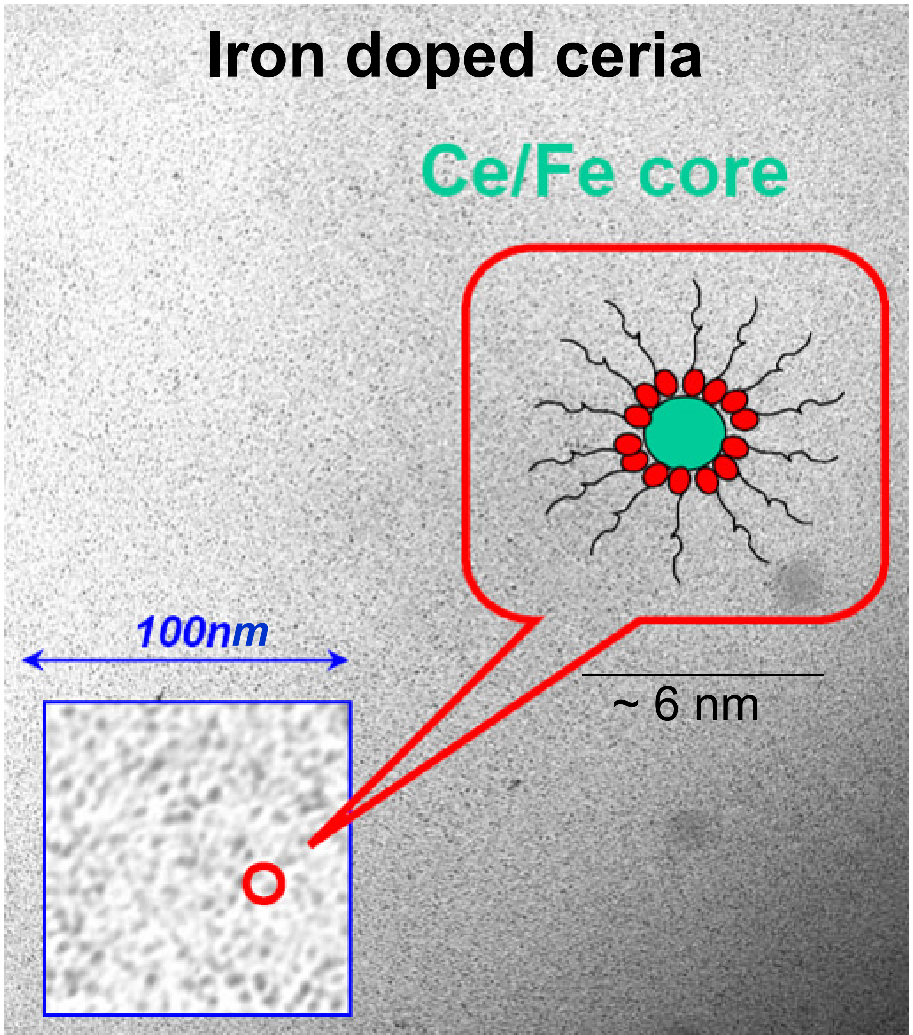


Comparison of sensitivity and dynamic working range for different analytical techniques

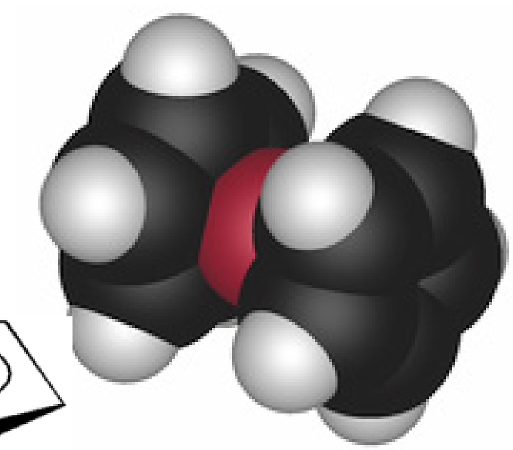


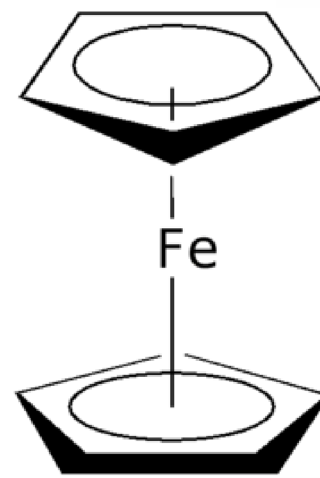
Types of fuel additives (FBC)

Nanoparticulate (additive fuel suspension)
versus organo-metallic additives (additive fuel mixture)



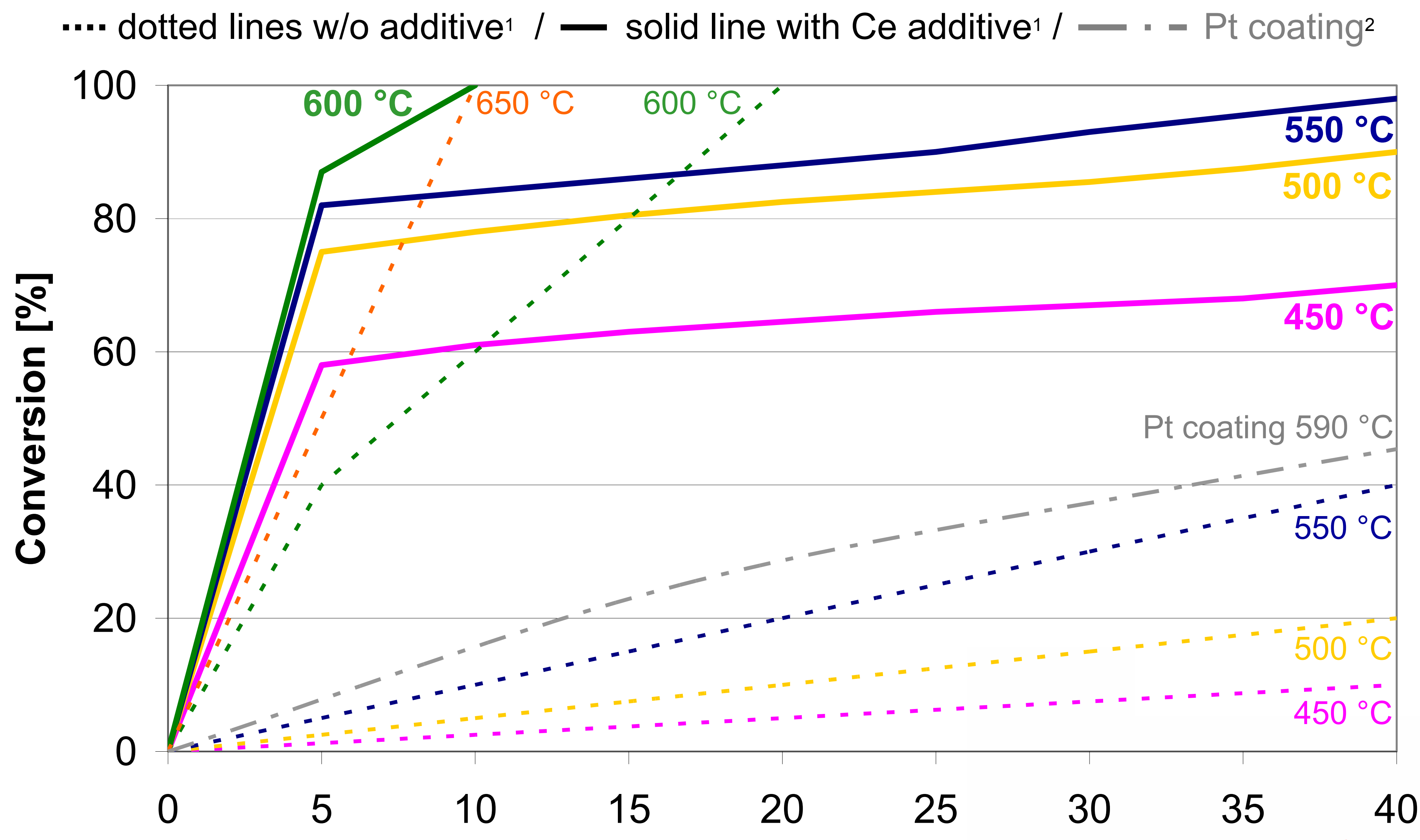
Ferrocene





Ferrocene

Effect of a metal additive on soot combustion



[1]Pierre Macaudiere *et al.* , AFS Conference 2003
[2]K. Ogyu et al., 2006-01-1526

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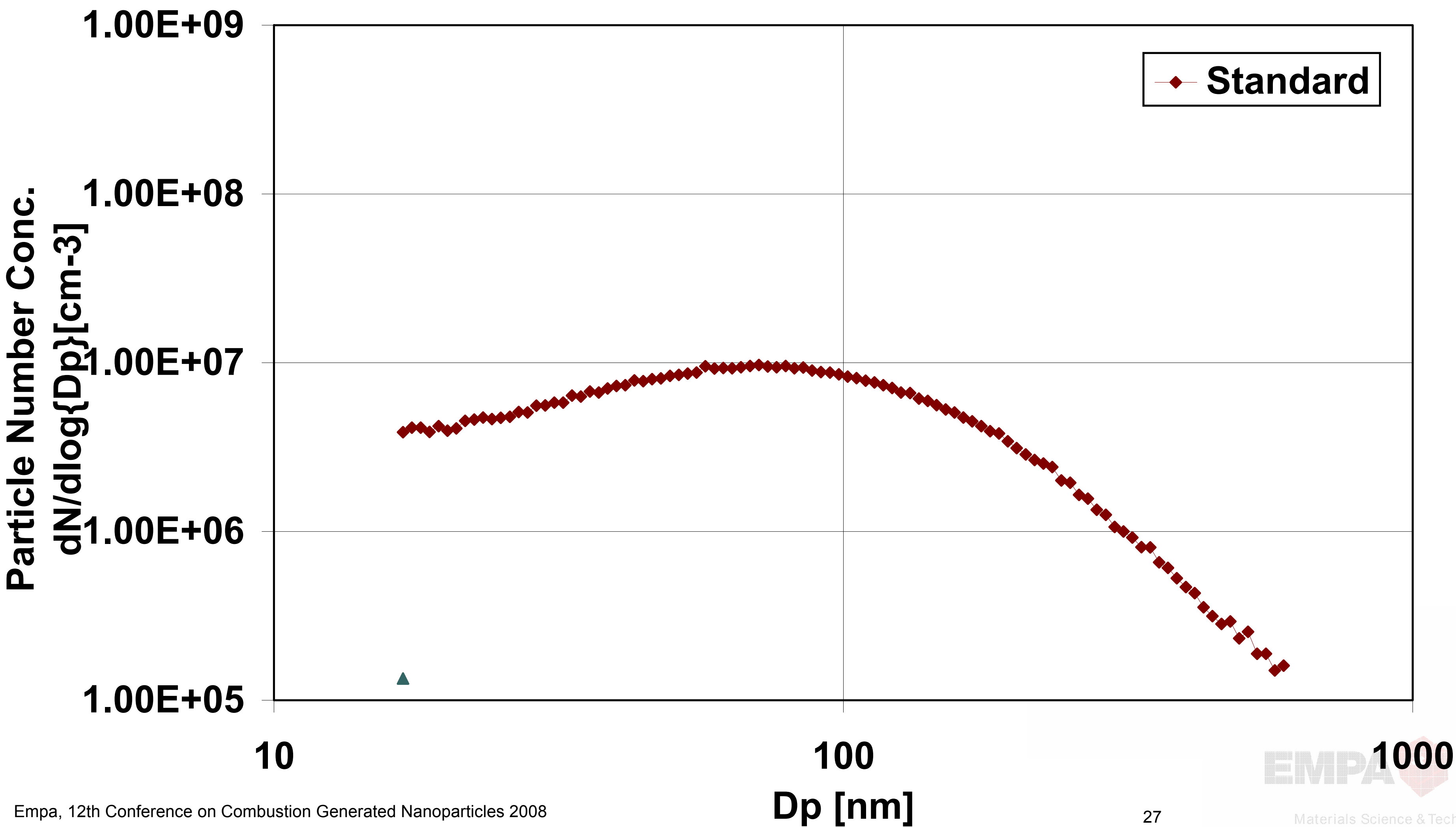
Materials Science & Technology

Effect of fuel additives on size distribution

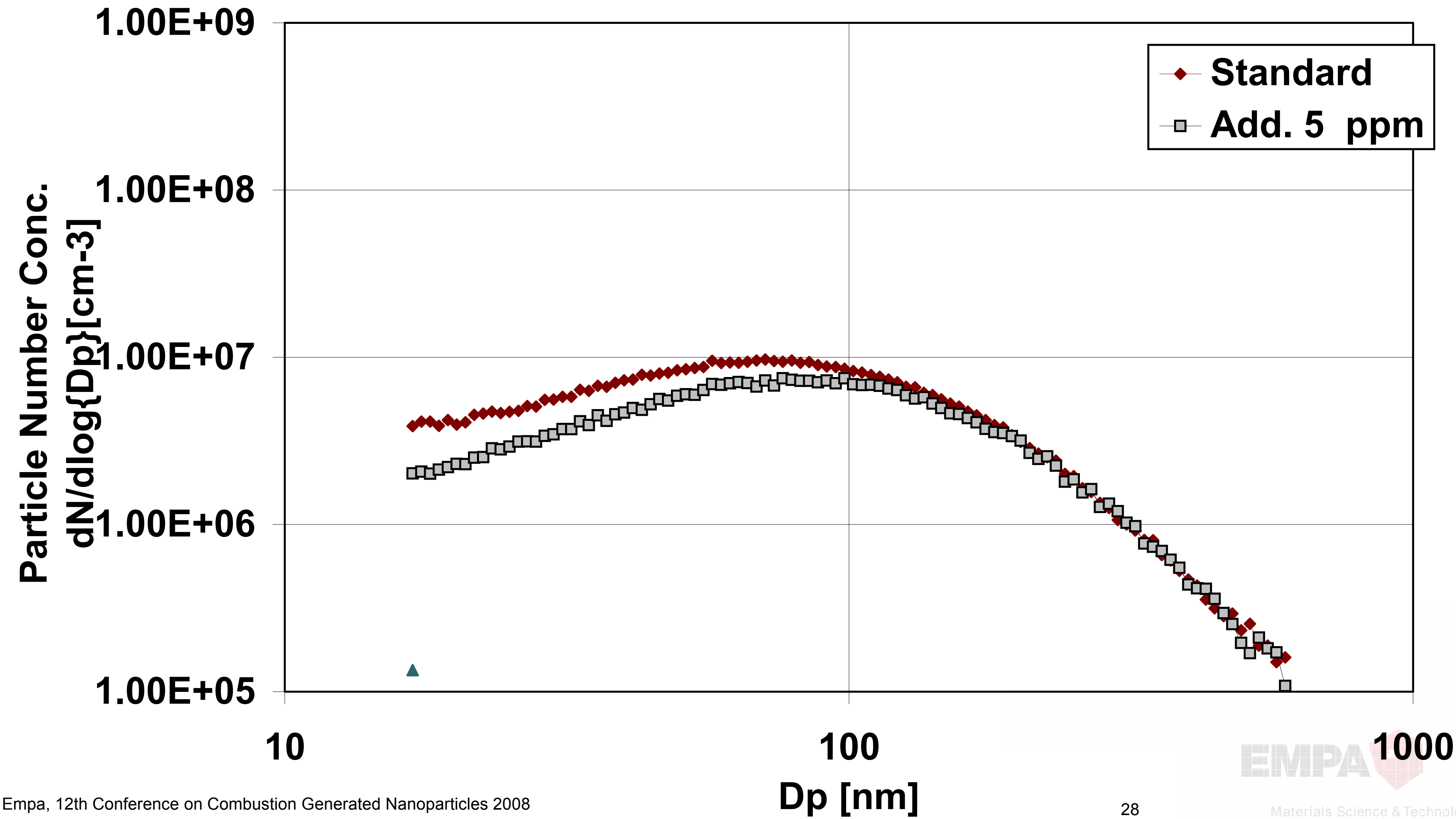
Standard Diesel

100 kW TDI Diesel Engine, 1400 rpm / 50 %Torque, SMPS



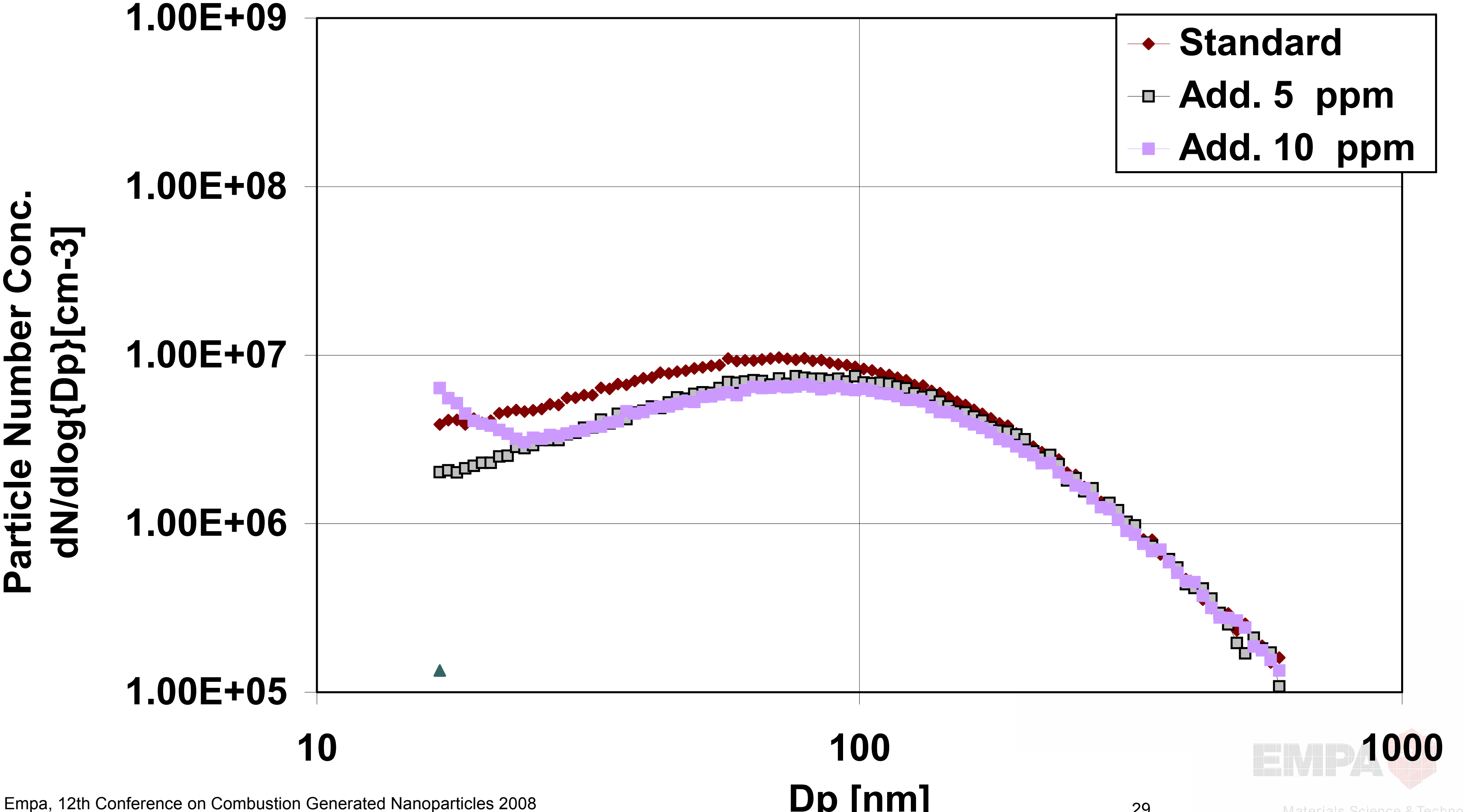
Effect of fuel additives on size distribution

Standard Diesel + 5 ppm Ceria Regeneration Additive
100 kW TDI Diesel Engine, 1400 rpm / 50 %Torque, SMPS



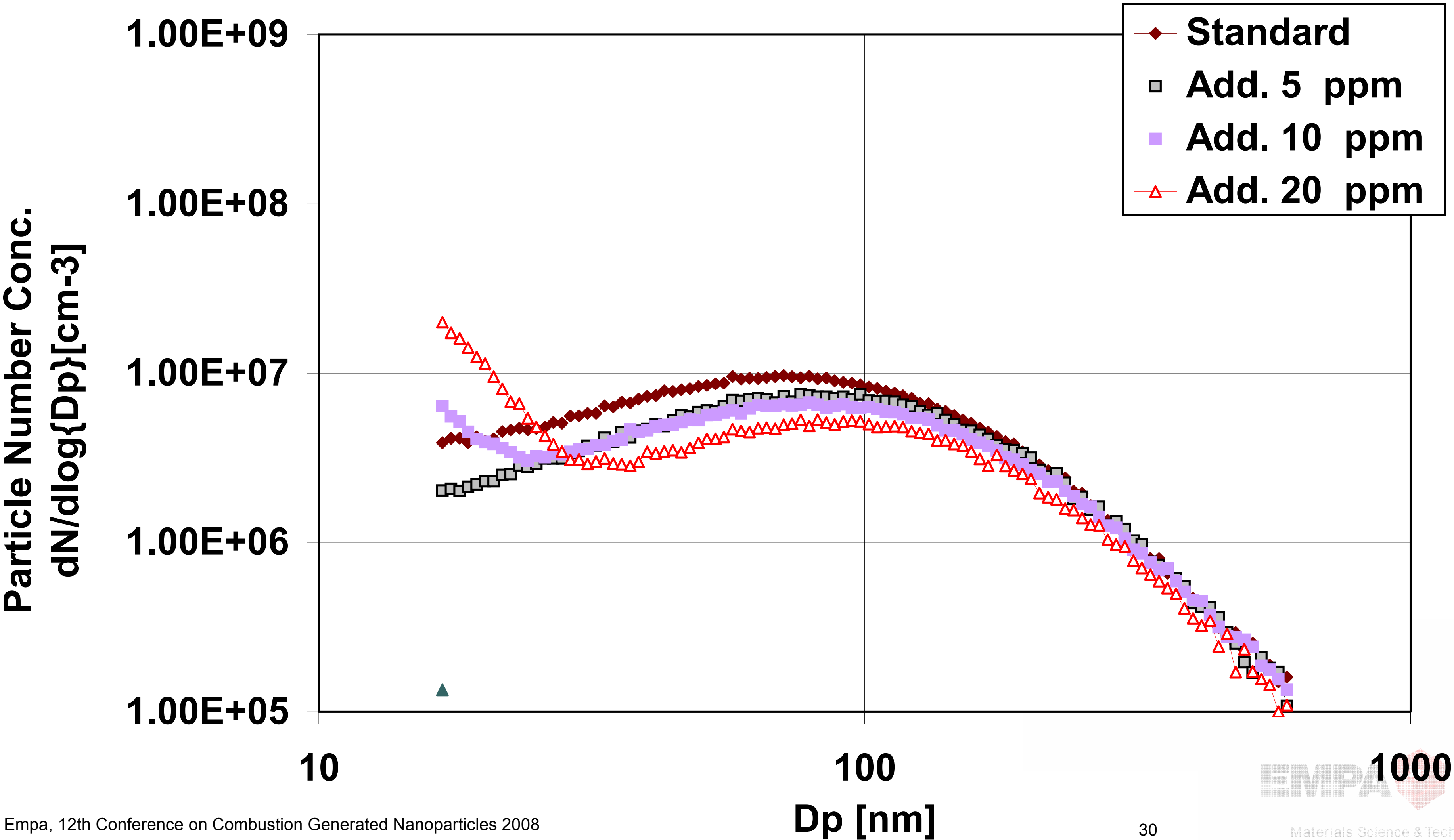
Effect of fuel additives on size distribution

Standard Diesel + 10 ppm Ceria Regeneration Additive
100 kW TDI Diesel Engine, 1400 rpm / 50 %Torque, SMPS



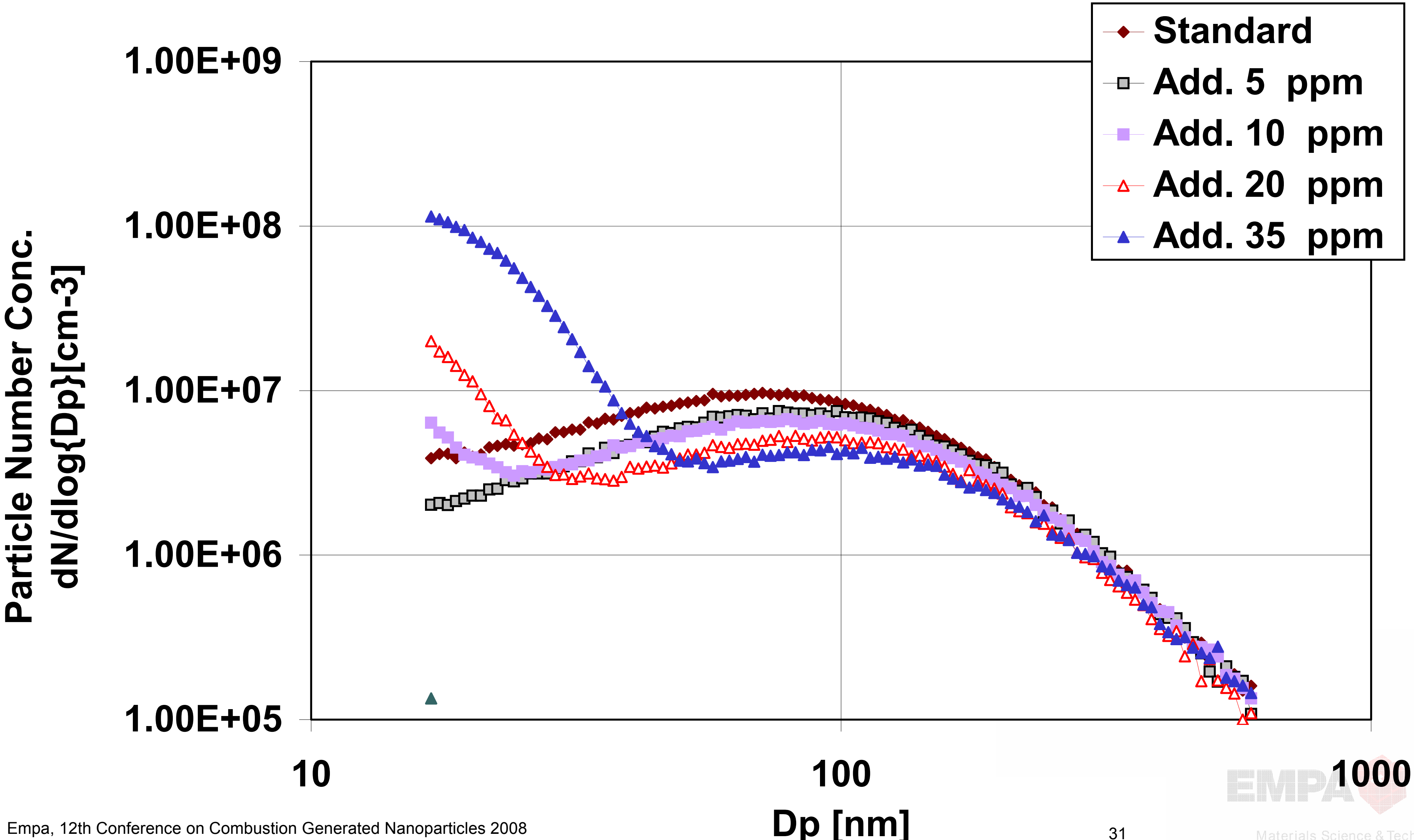
Effect of fuel additives on size distribution

Standard Diesel + 20 ppm Ceria Regeneration Additive
100 kW TDI Diesel Engine, 1400 rpm / 50 %Torque, SMPS



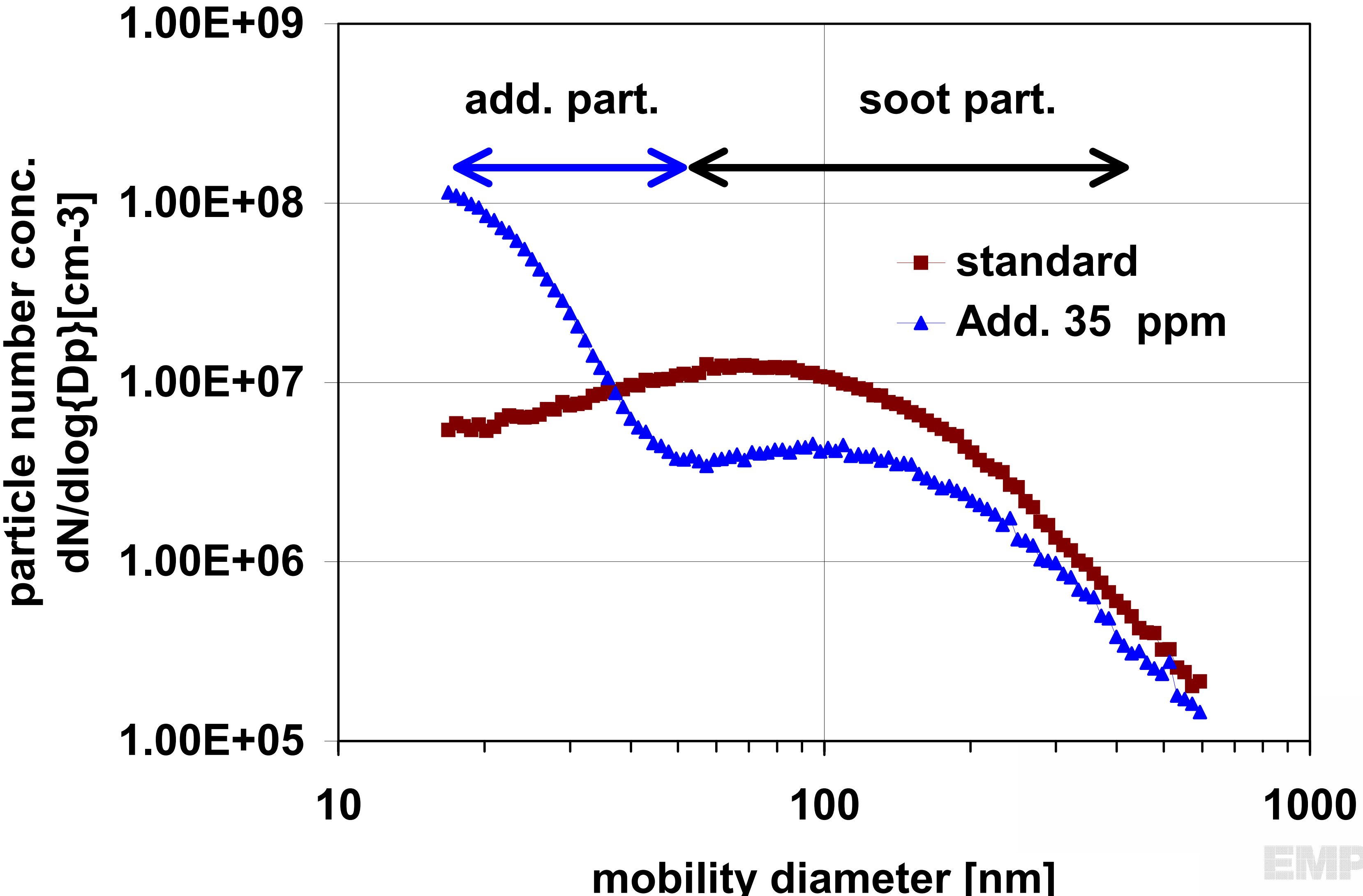
Effect of fuel additives on size distribution

Standard Diesel + 35 ppm Ceria Regeneration Additive
100 kW TDI Diesel Engine, 1400 rpm / 50 %Torque, SMPS



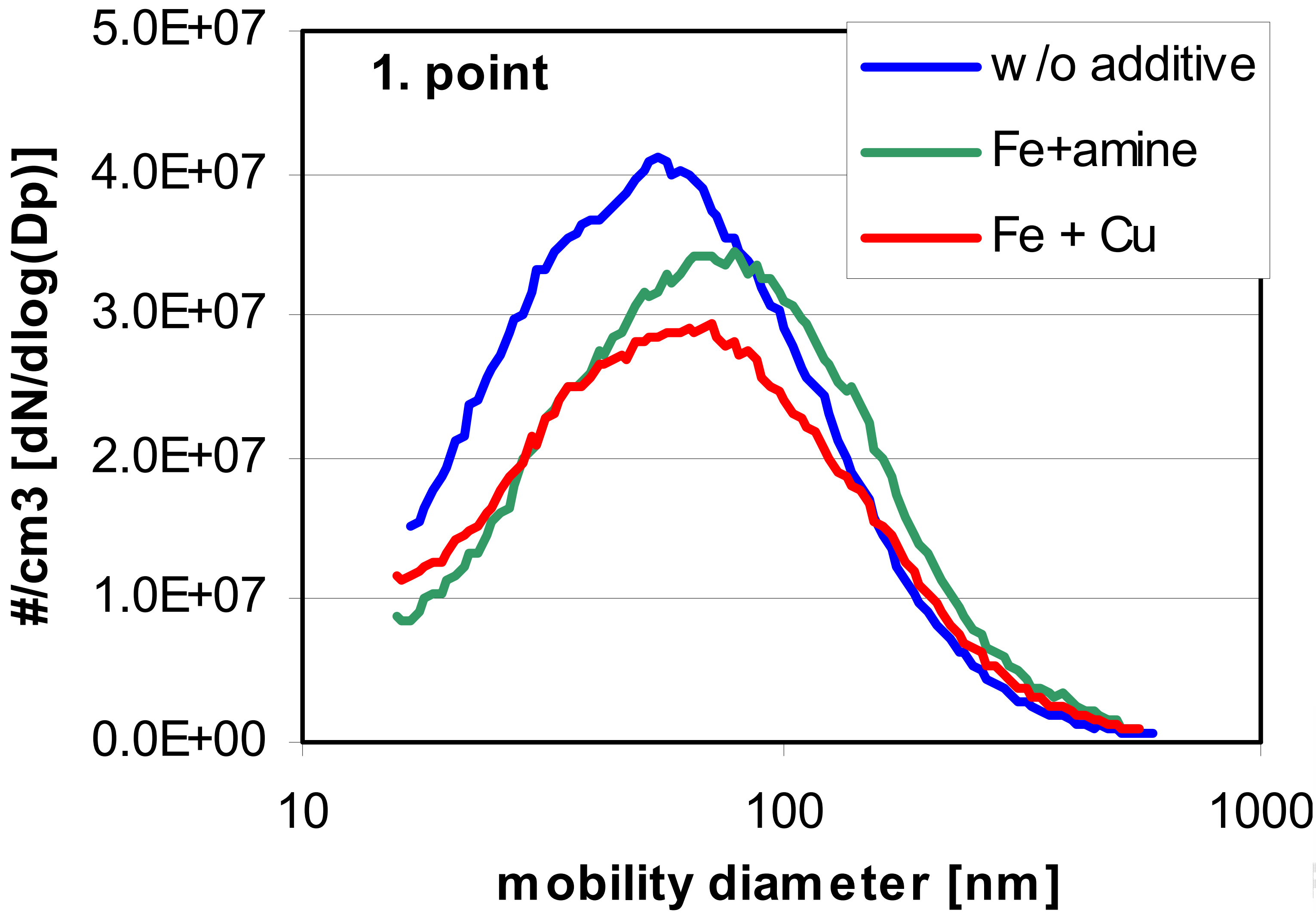
Effect of fuel additives on size distribution

Standard Diesel + 35 ppm Ceria Regeneration Additive
100 kW TDI Diesel Engine, 1400 rpm / 50 %Torque, SMPS



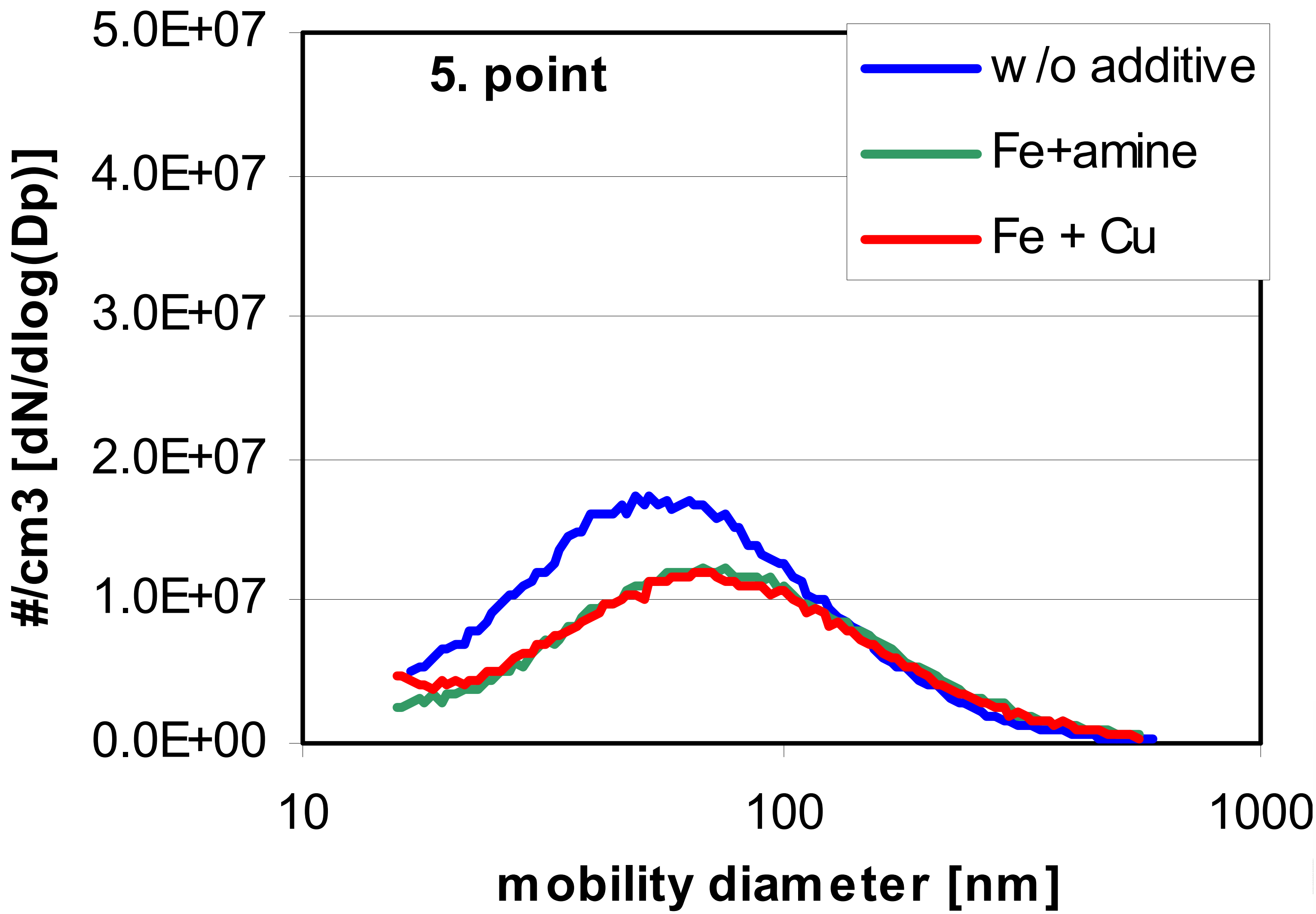
Effect of fuel additives on size distribution

5 ppm Fe + 31ppm C8 amine // 5 ppm Fe + 5 ppm Cu regeneration additives



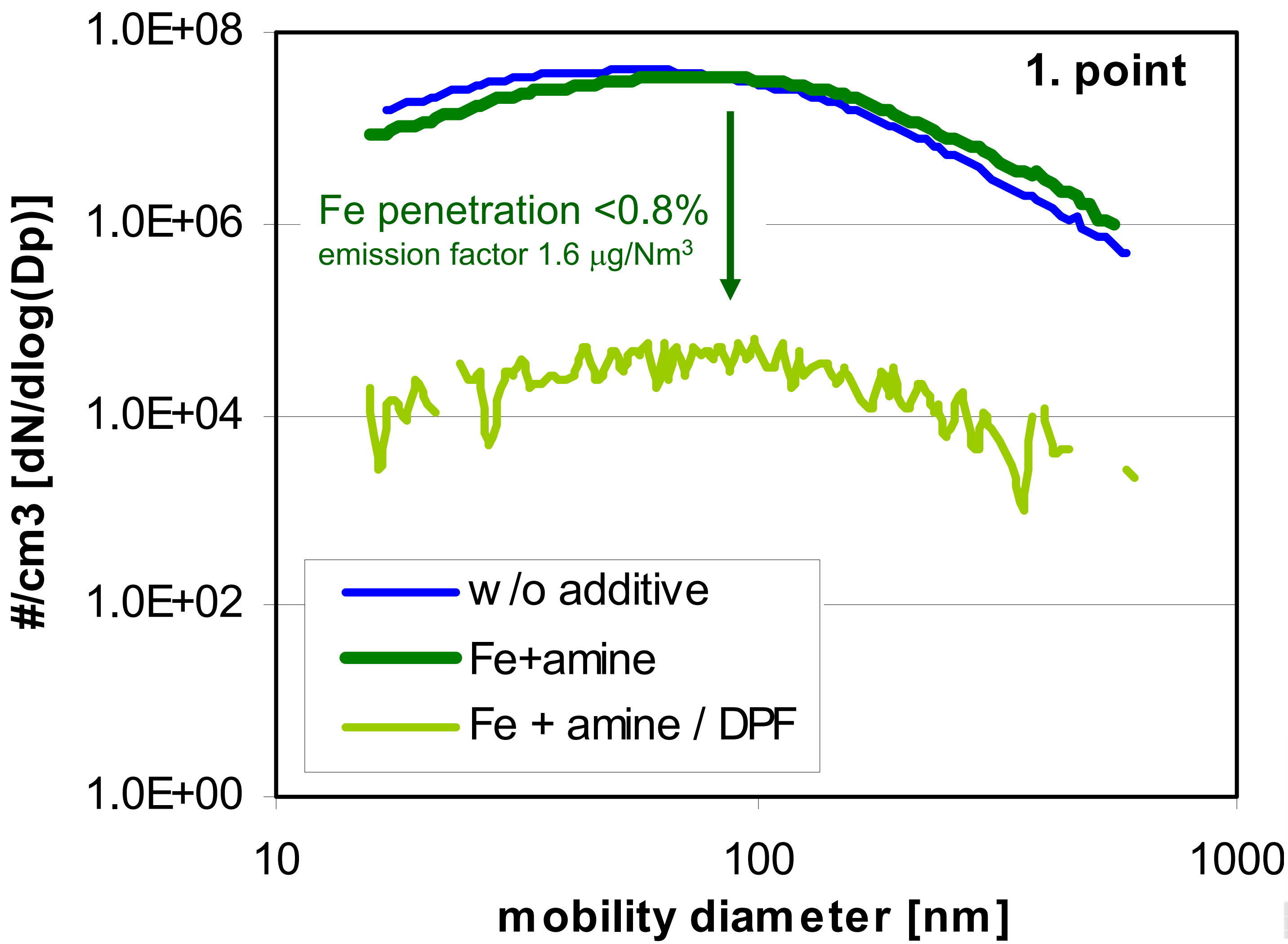
Effect of fuel additives on size distribution

iron/amine and iron/copper regeneration additive



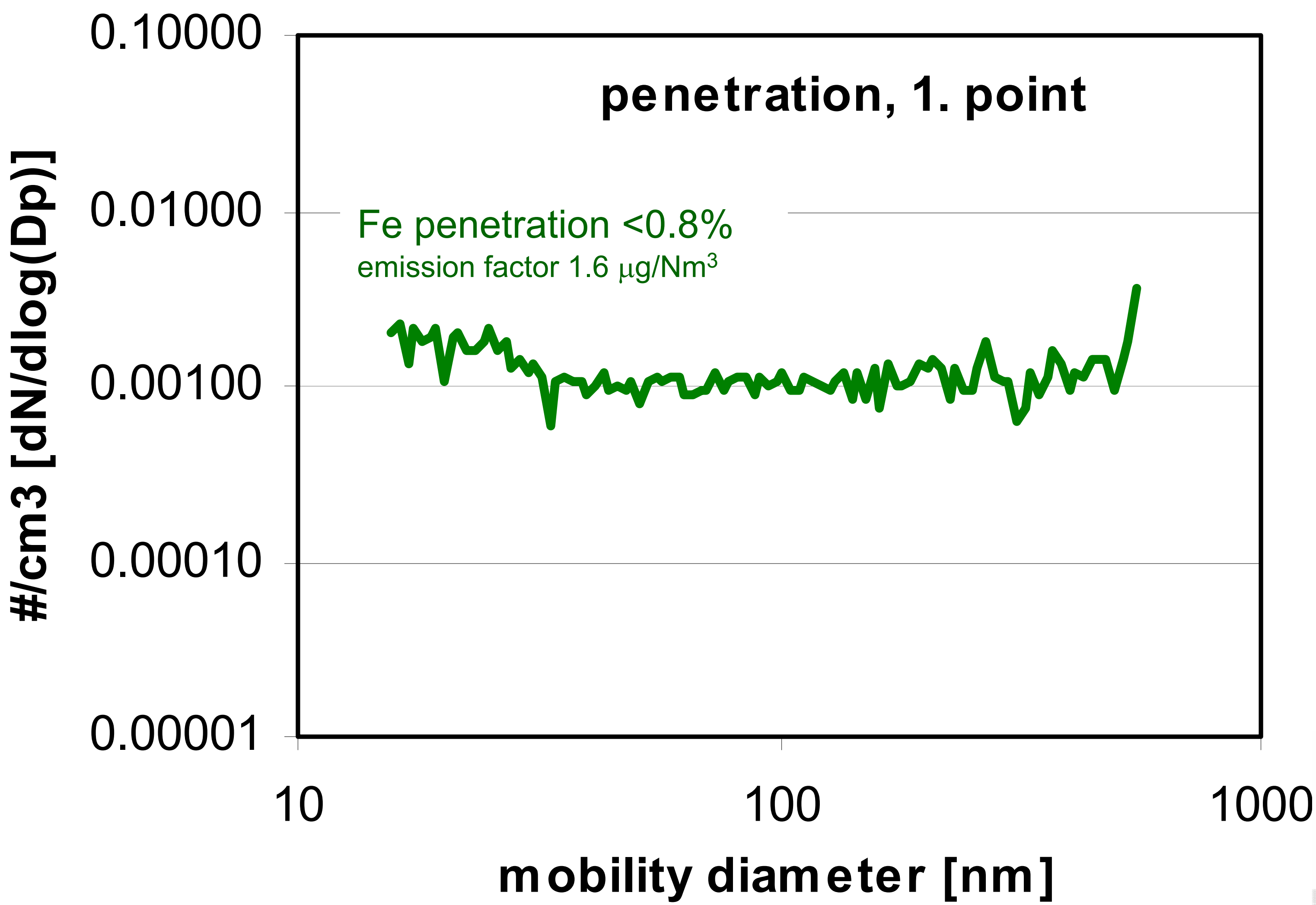
Effective retention for FBC in the DPF

Fe/amine additive



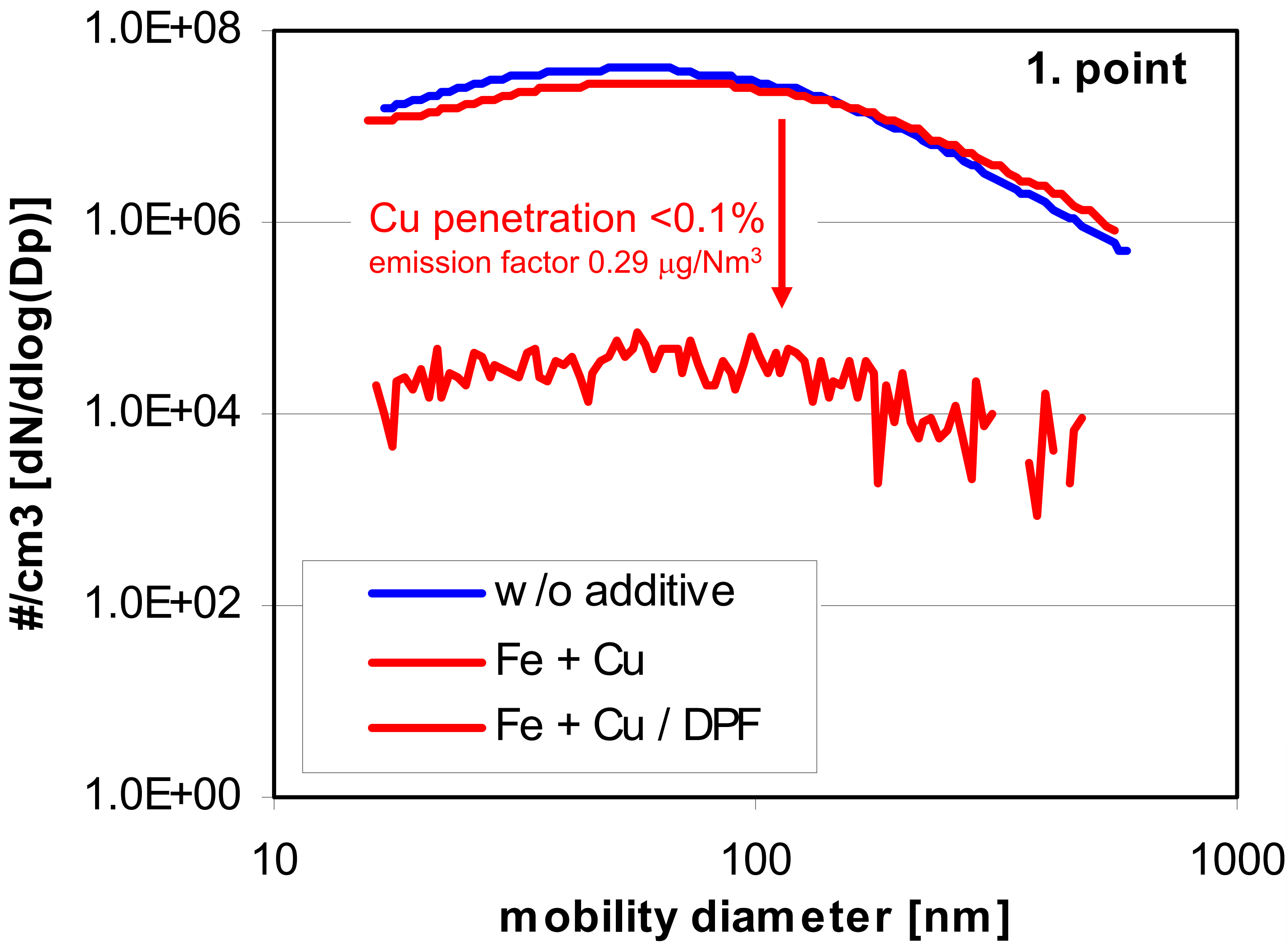
Effective retention for FBC in the DPF

Filtration effectivity >99 %



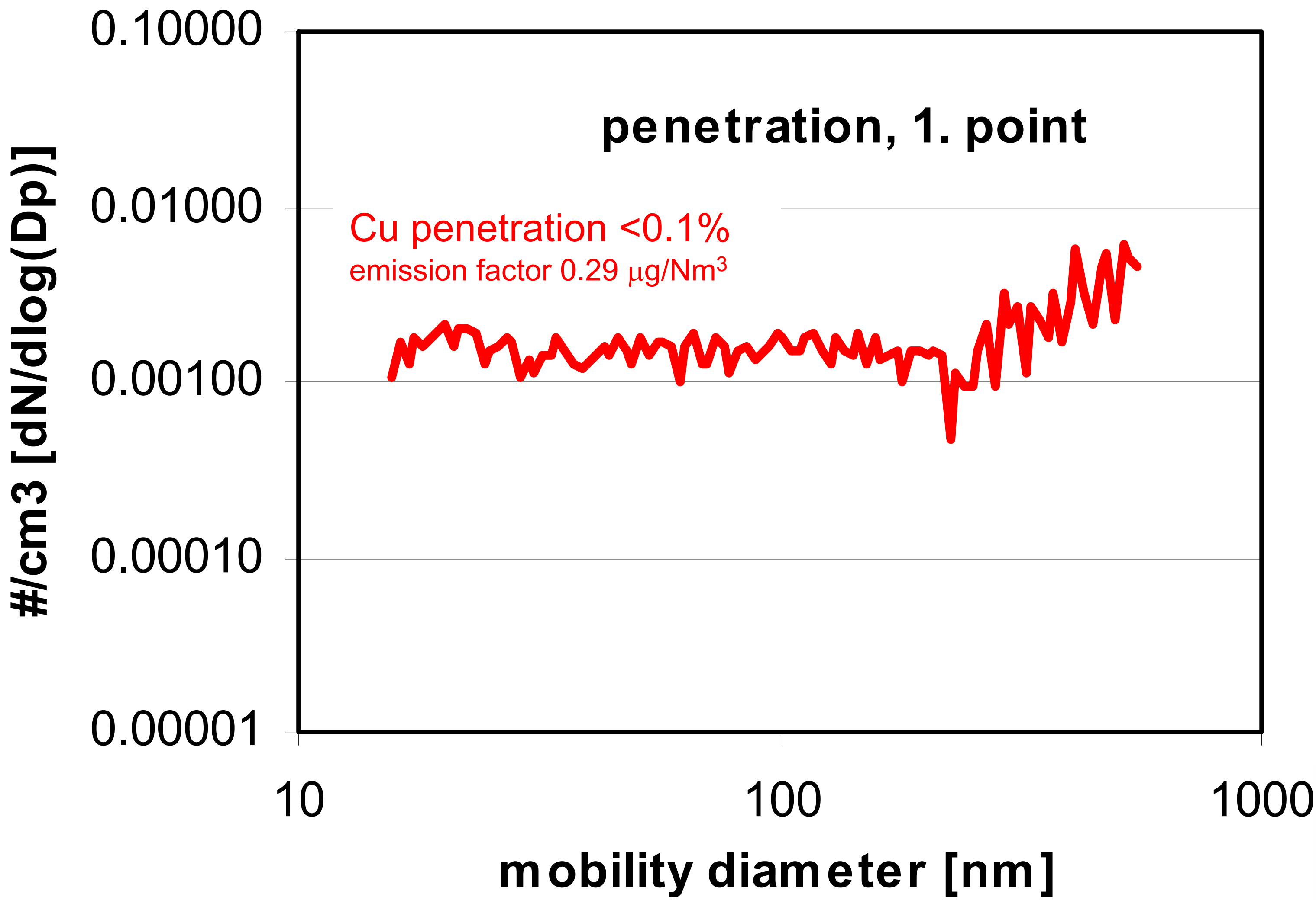
Effective retention for FBC in the DPF

Fe/Cu additive



Effective retention for FBC in the DPF

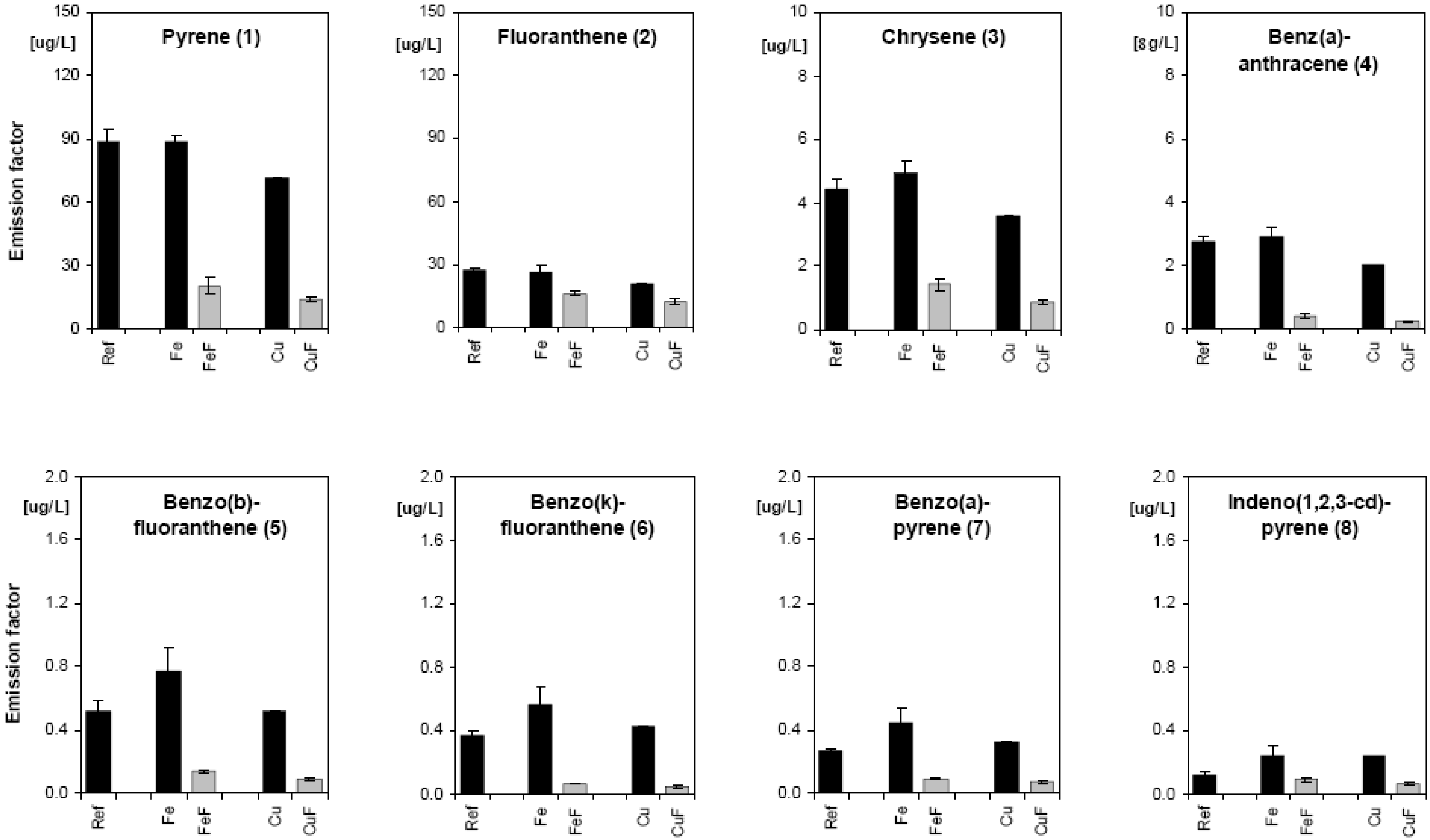
Fe/Cu additive



Potential of DPF to reduce toxic components

e.g. PAHs / Toxicity

Talk N.V. Heeb

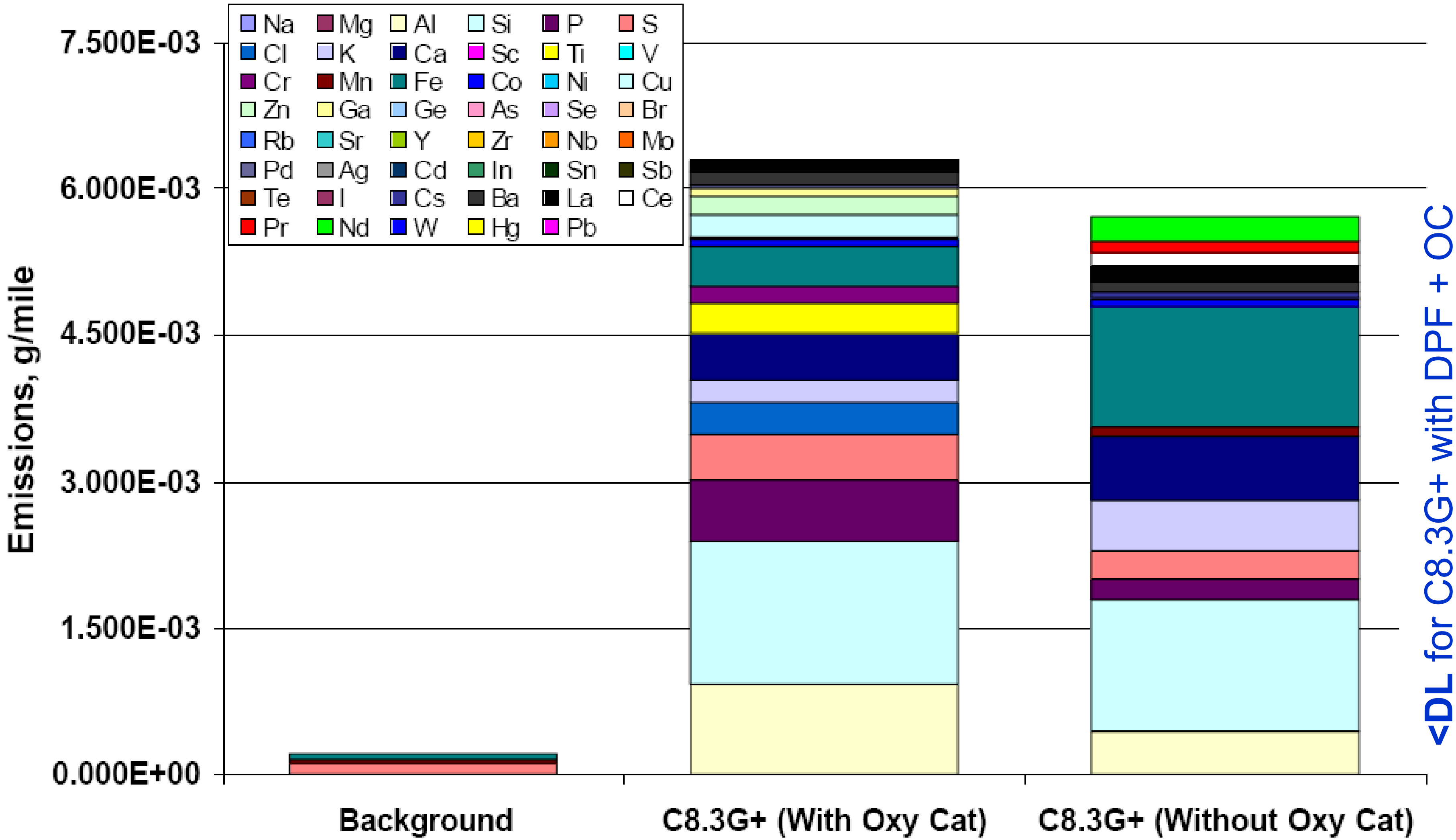


N. V. Heeb *et al.,* Environ. Sci. Technol. 42 (10), 2008 3773 – 3779.
D. Wenger *et al.,* Environ. Sci. Technol. 42(8); 2008; 2992-2998.

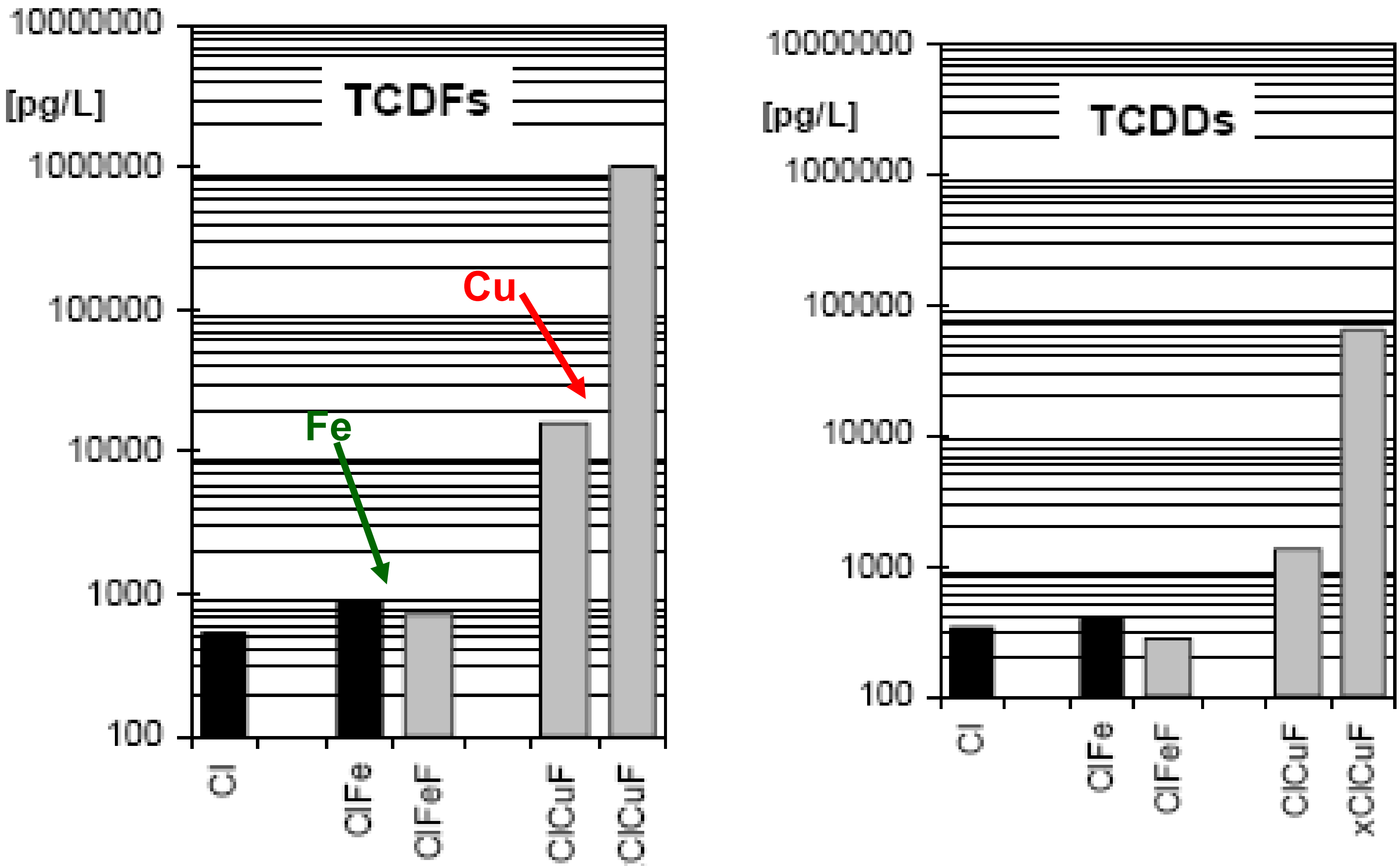
Metall emissions determined by XRF

Oxidation catalyst (OC) versus DPF with OC

M. Gautam et al. Chemical characterization of PM emissions from a catalyzed trap equipped natural gas fueled transit bus, ETH Conference on Combustion Generated Nanoparticles 2007



Effect of metallic fuel additives on formation of secondary emissions e.g. Dioxin with Cu

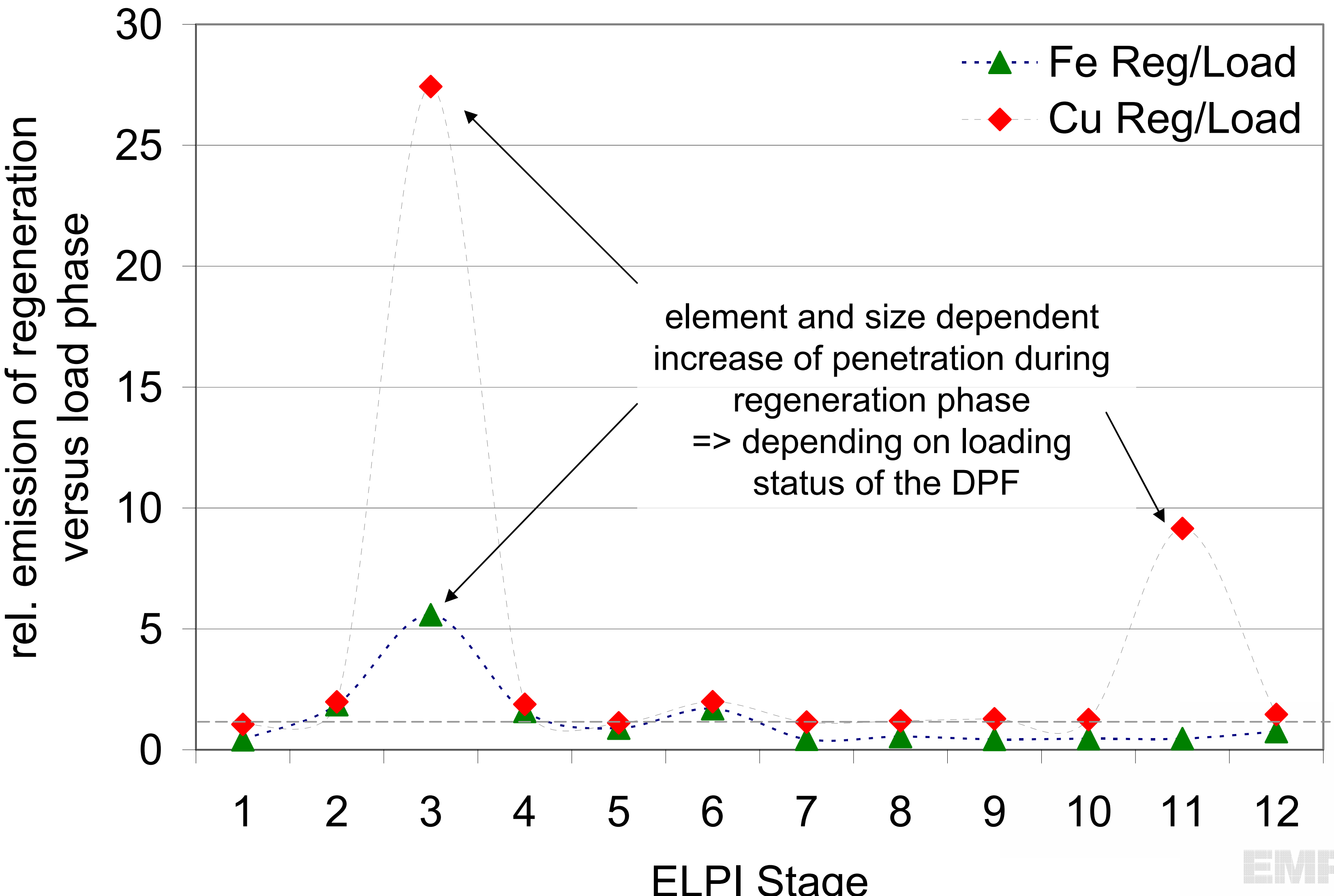


N.V. Heeb, Environ. Sci. Technol.; 2007; 41(16); 5789-5794.

N.V. Heeb et al., ETH Conference on Combustion Generated Nanoparticles 2007

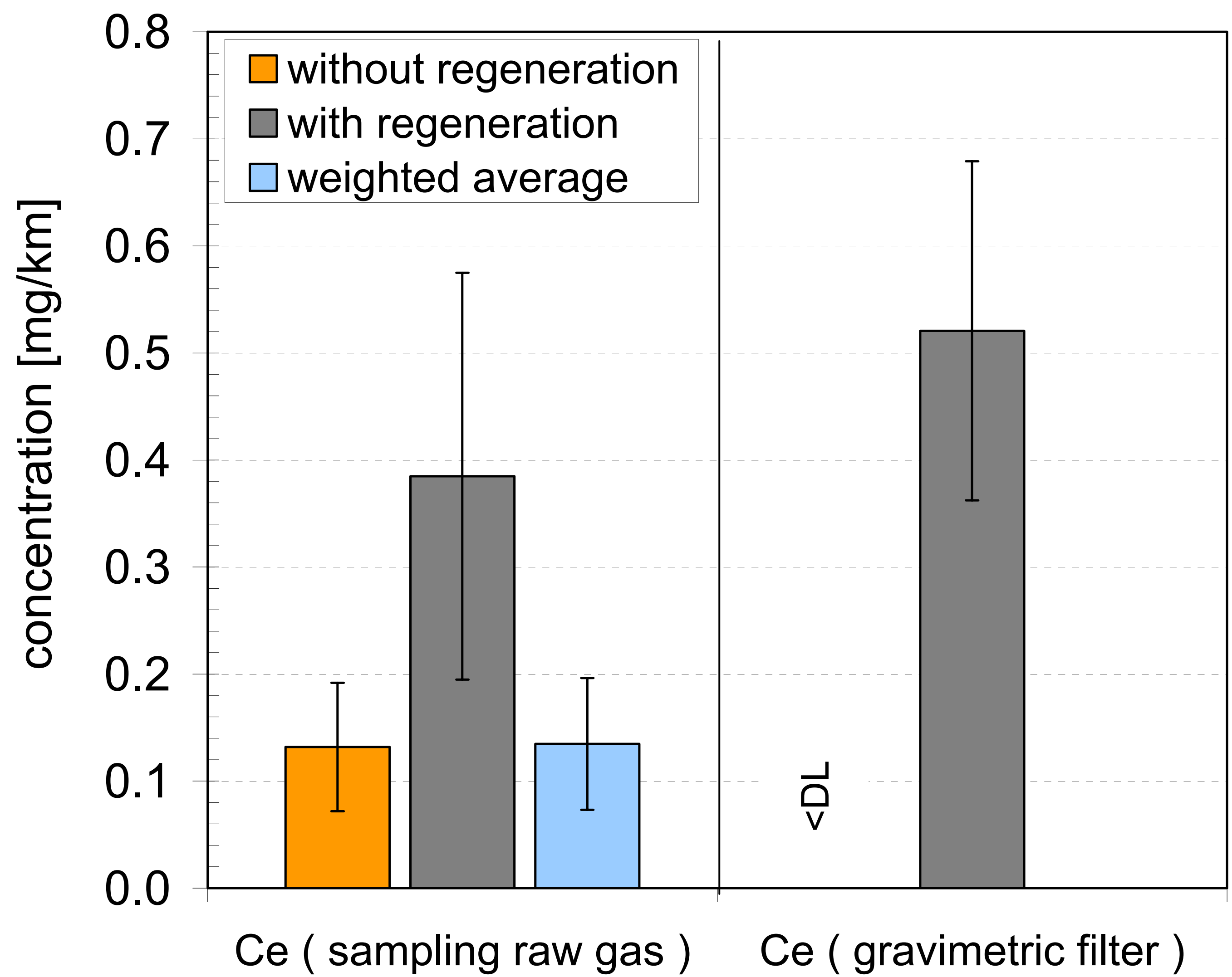
Is there a difference in penetration of FBC during regeneration phase compared to loading phase?

Relative enhancement of emissions during DPF regeneration phase for a Fe/Cu additive



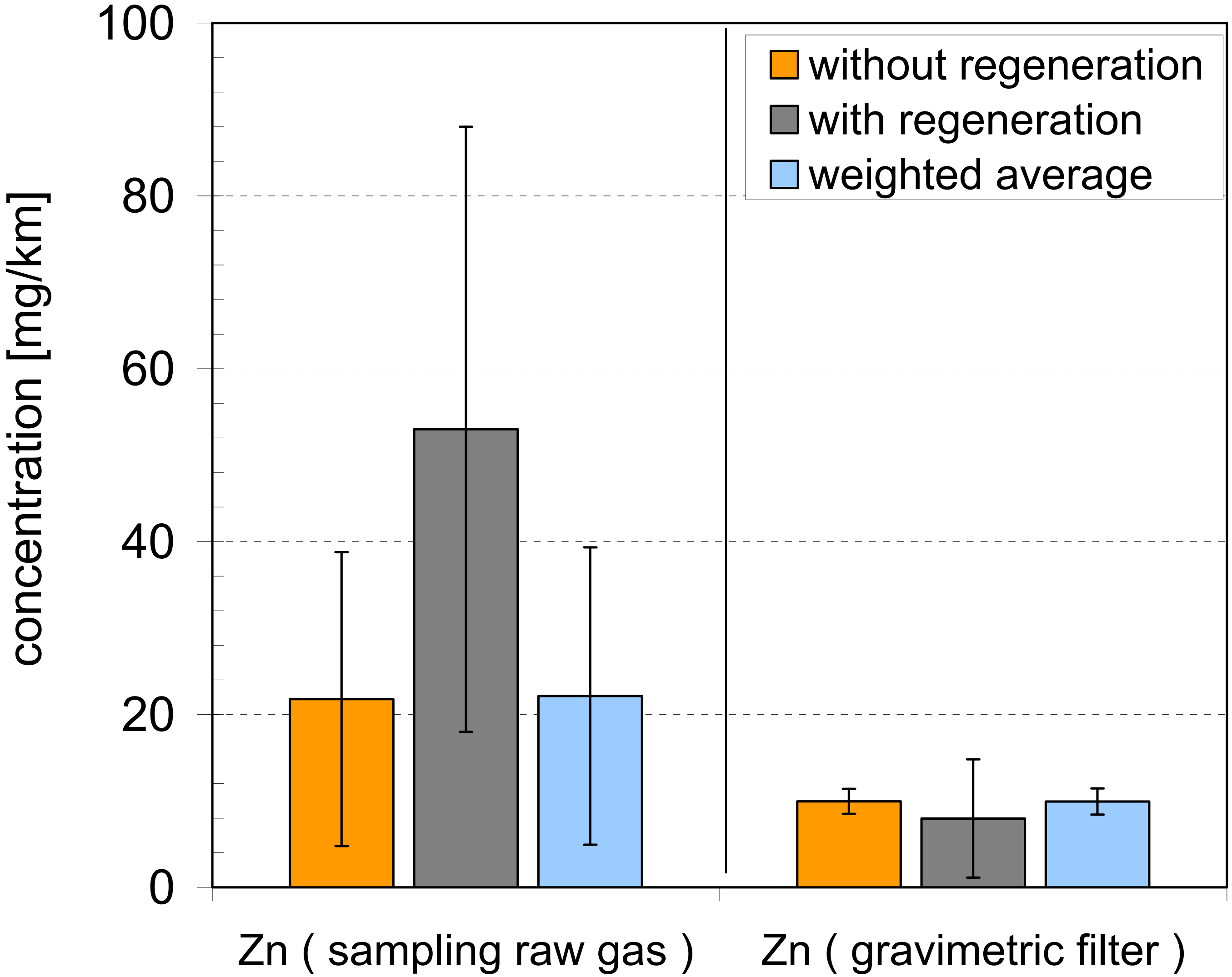
Loading versus Regeneration phase

Ceria Regeneration Additive – Possible Penetration of the Additive Metal Ce



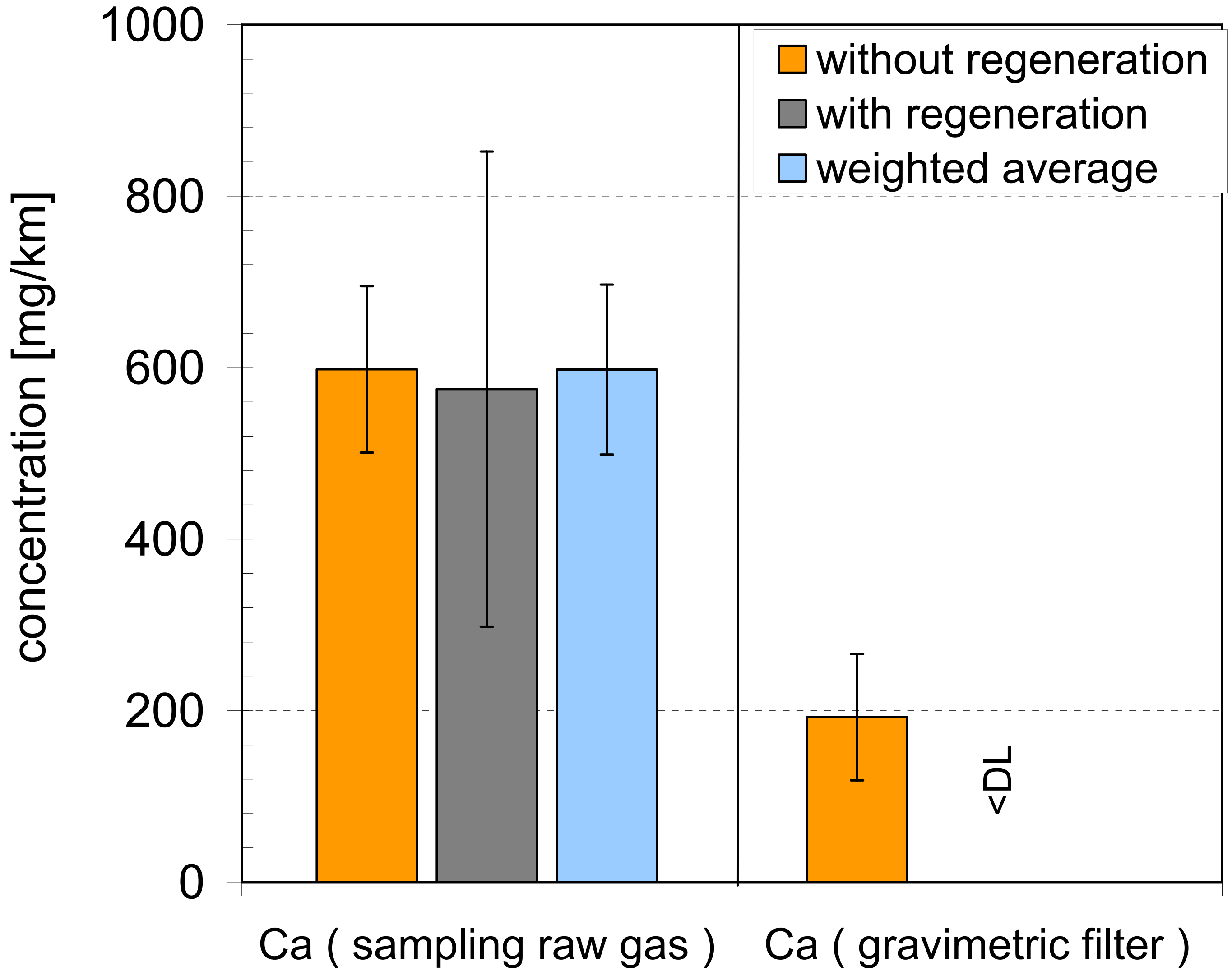
Loading versus Regeneration

Ceria Regeneration Additive – Possible Release of Stored Metals e.g. Zn



Loading versus Regeneration

Ceria Regeneration Additive – Possible Release of Stored Metals e.g. Ca



Advantages and Disadvantages of DPF

- High filtration efficiency for particle (> 99 % can be achieved)
- Reduction of toxic and carcinogenic components e.g. PAHs, metals
- Hazard of formation of secondary emission
  Cu (e.g. FBC) supports Dioxin formation, Pt coating tends to sulphur accumulation
- Possible deposition of FBC in the engine (precipitation)
- Fuel additive can change size distribution of emission
- Enhanced penetration of FBC during regeneration phase depending on the loading status of the DPF
  (penetration of catalytic metal additive and release of stored metals)
- Contribution of penetration during regeneration is low when short regeneration time is taken into account
  (if DPF ageing effects further increase needs to be checked)

Outlook – Further Investigations

- Localization of additive deposition (engine, exhaust pipe, CVS)
- Does an “initial deposition phenomenon exists? (later release?)
- Long-term stability of additive fuel mixtures (Influence of additive and fuel composition, homogeneity of mixture, temperature stability)
- Influence of lubricants
- Further investigations on the DPF operation conditions loading and regeneration phases (fuel additives, coating)
- Retaining of metals in the DPF (possible release during regeneration?)
- Storage and release effects (e.g. sulphur)
- Long-term behaviour of DPF on penetration or abrasion (aging)
- Comparison of different concepts (DPF + FBC; coated DPF)

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