Quantifying Pt Emissions from Pt Based FBCs with DPF's

13th ETH Conference onCombustion Generated Nano paticles

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Pt emission literature study

- The health implications of low-level platinum exposures are not fully understood.
- The metallic form of Pt is generally considered inert as regards biological reactions (Ravindra et al 2004).
- It is known that “soluble” negatively charged complexes are significantly more allergenic than elemental or oxide species.
- Soluble Pt salts are considered highly toxic (OSHA exposure limits of 2 µg m-3 (TWA: 8-hour/day, 40-hour/week). Elemental platinum, Pt0, is much less toxic and recommended external exposure limits reflect this difference (NIOSH/TWA: 1000 µg m-3).

Catalysts are an essential part of any emission control

Traditional catalyst

- Single phase catalytic activity
  - ✓ Solid state
- Treats exhaust stream after leaving engine
- High Pt loadings = High NO2
- Subject to long-term degradation in performance

Platinum/Cerium based fuel-borne catalyst

Unique triple-phase catalytic activity

- ✓ Solid state
- ✓ Liquid state
- ✓ Gaseous state

- For use with full-flow DPF systems only
- Catalytic action begins in combustion chamber
- Continues through control device
- Low Pt concentrations = no additional NO2
- Lower life time use of Pt by up to 50%

Platinum Characterisation

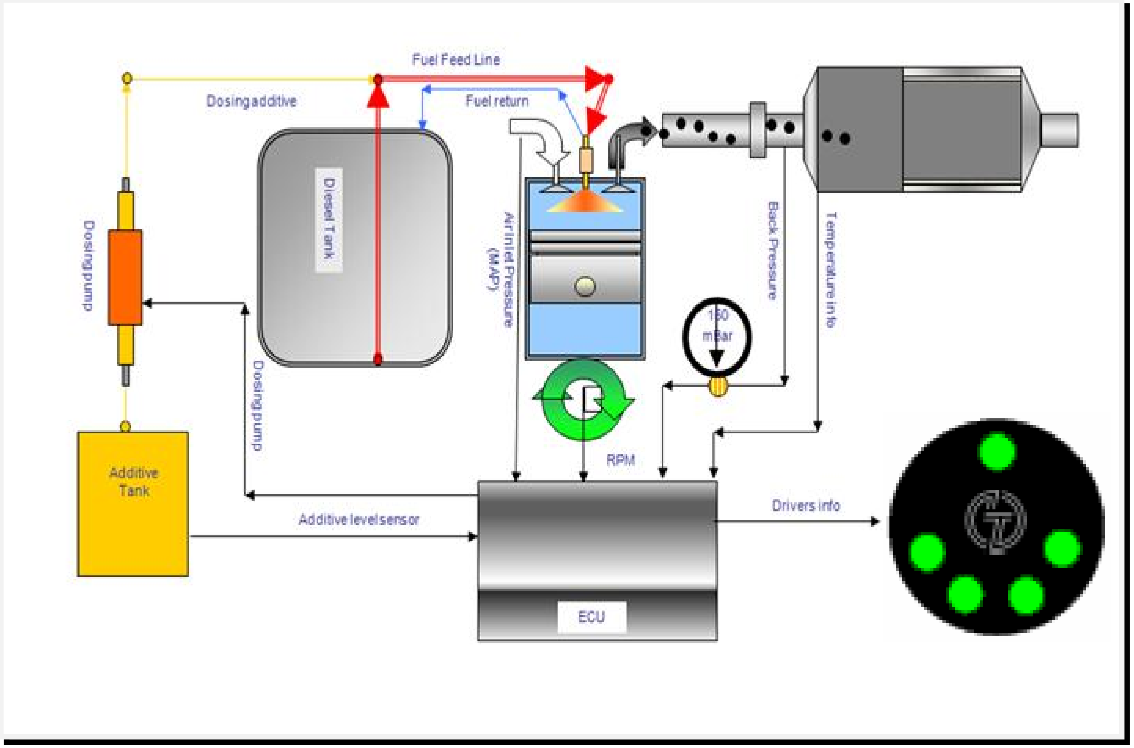
- Platinum emitted from a solid catalyst is largely present as elemental platinum adhered to large (>10 micron) size particles composed of ceramic matrix substrate from the catalyst surface.
- Platinum emitted from an engine operating on fuel containing Platinum Plus exists in a micron or submicron size particle in a complex organic matrix (i.e., diesel soot).
- Previous testing for VERT approval established Pt emissions derived from the FBC did not show as a separate peak in the SMPS (reference VERT VSET approval B083 Platinum Plus DFX-DPF)

Environmental Agencies

- US Environmental Protection Agency – Registration list for Fuel additives
- Transport for London – LEZ approved technologies List
- German *Umweltbundesamt* UBA – KBA
- VERT – BAFU and SUVA Approved additives list
- Singapore – LTA and NEA
- China – EPA
- Californian Air Resource Board - Multimedia Assessment

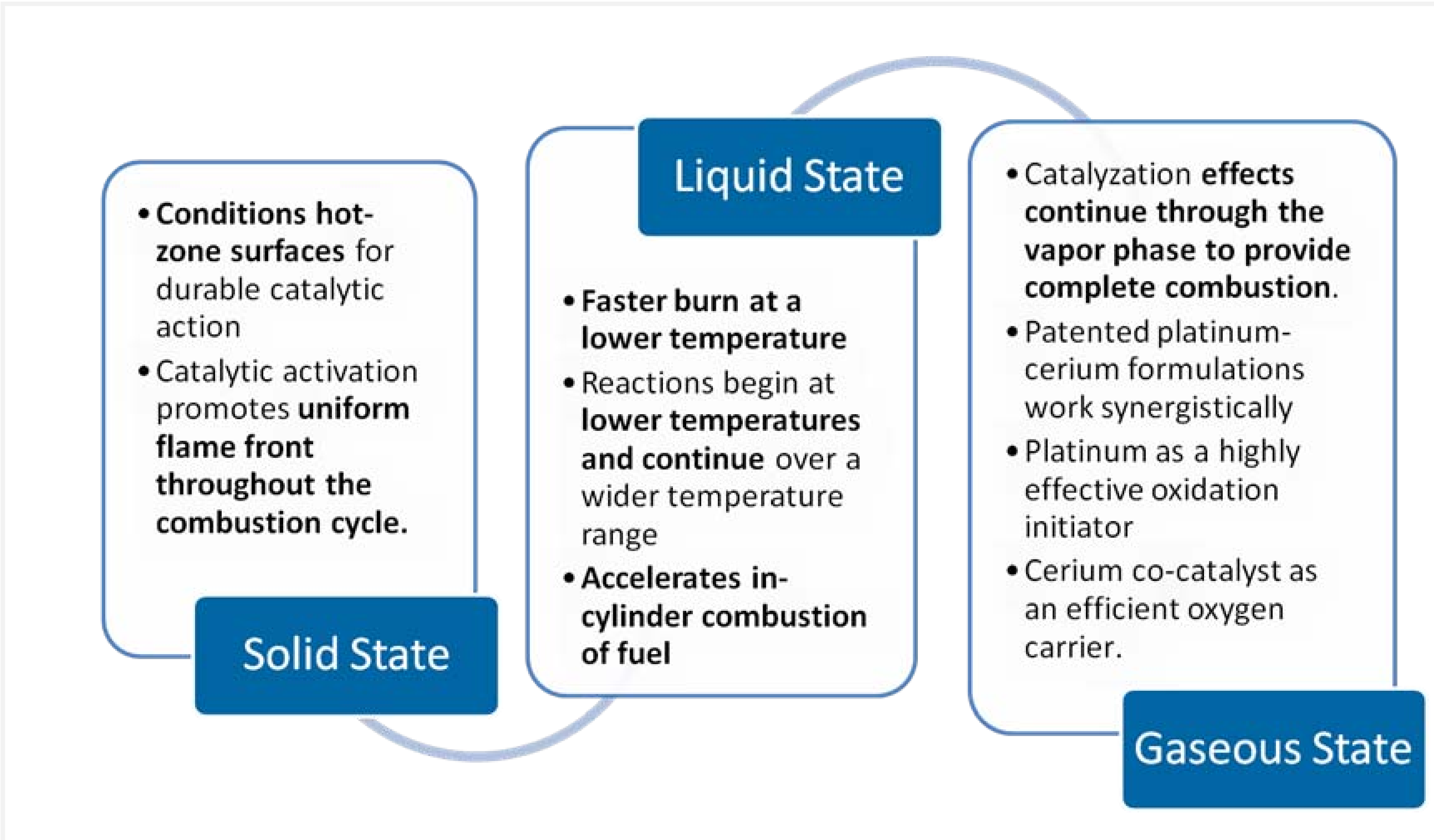
FBC delivery and diagnostic system

- Accurate injection of Pt/Ce FBC for efficient DPF regeneration
- Monitor and data log operational data
- System and Maintenance diagnostics feedback via dashboard indicator.
- Fully programmable dosing system
- Error and Alarm data logging
- Remote Communication



- Programmable Electronic Control Module
- ECU Programming and Interface Software
- Fuel Additive Pump
- Operator Condition and Warning Indicator
- Back Pressure and Temperature

Pt based FBC - Three phase catalytic activity



Longterm use of Pt/Ce FBC - VERT VFT3 test

Summary results after 2000 hrs (Reference VERT VFT3 No B211)

- Liqtech Silicon Carbide Filter
- Platinum Plus DFX DPF FBC delivers 0.5 ppm Pt and 7.5 ppm Cerium into the fuel
- The DPF was very efficient even after 2000hrs the filtration of solid nanoparticulates was up to 99.2 %
- The regeneration of the DPF with fuel additive (FBC) worked very well
- Due to the catalytic residues after field test and the effect of FBC there is efficient elimination of CO & HC, but no increase of NO_2

“DPF DAUGBJERG Scan-Filter Systems TH 941 with Platinum Plus DFX DPF - fulfils the criteria of the VERT filter test phase 1, 2 and 3”.

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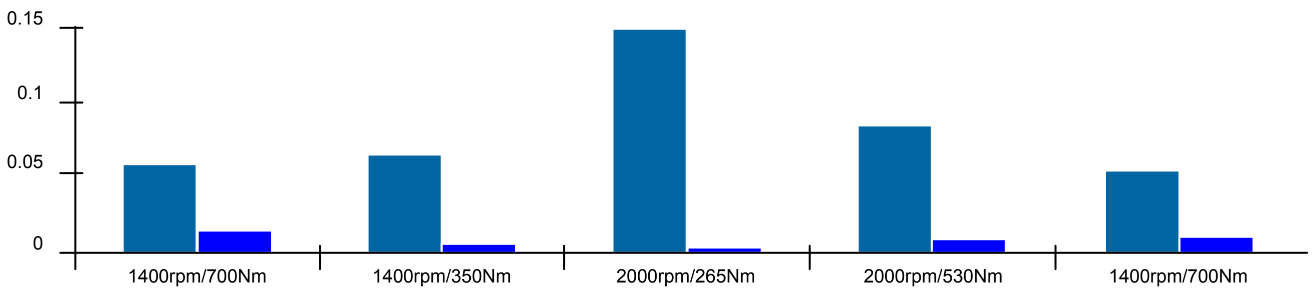
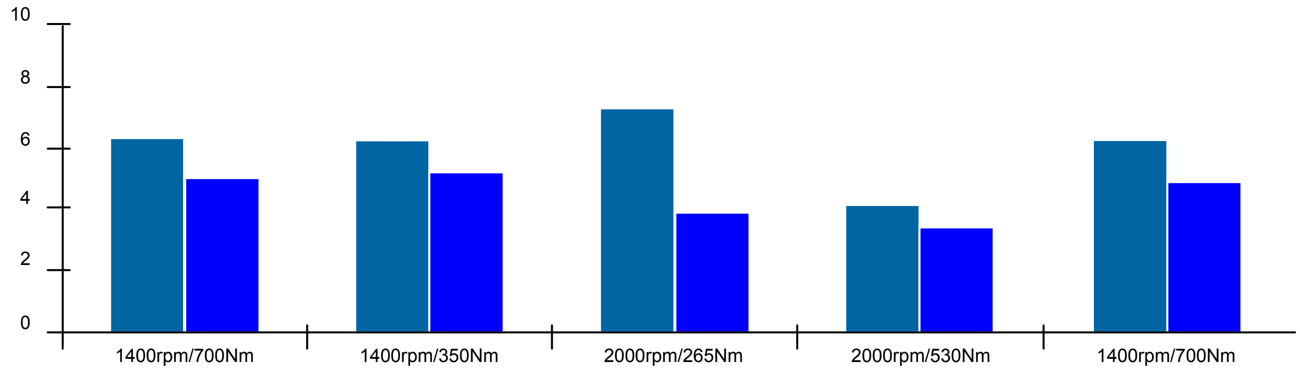
VERT VFT3 – Results after 2000 hrs Use



PM_{engine} [g/kWh]

without DPF (reference)

DPF after 2000 h



$NO_{X\ (hot)}$ [g/kWh]

without DPF (reference)

DPF after 2000 h

engine: Liebherr D 934 S A6;
fuel: ulsd (S<10 ppm)

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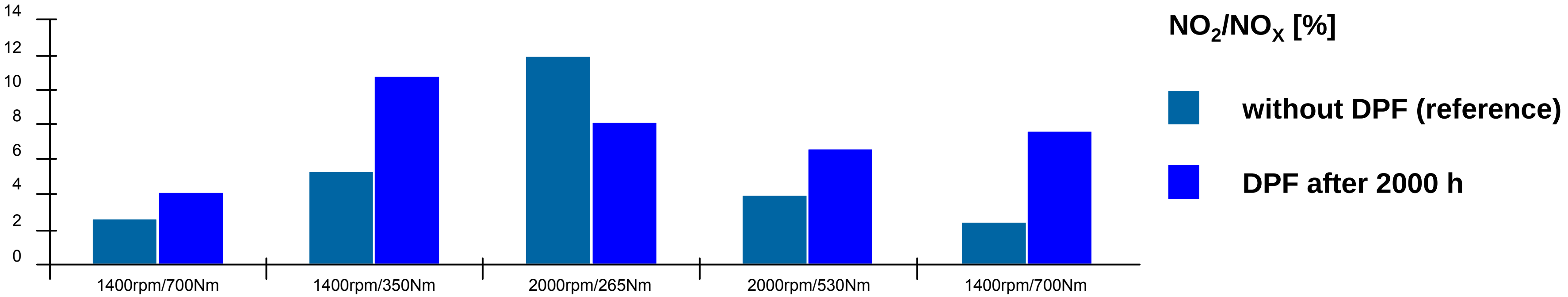

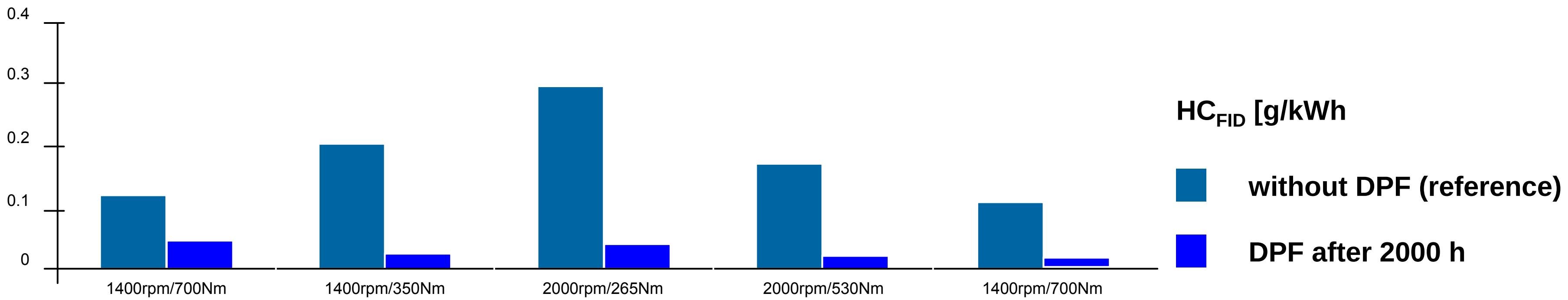

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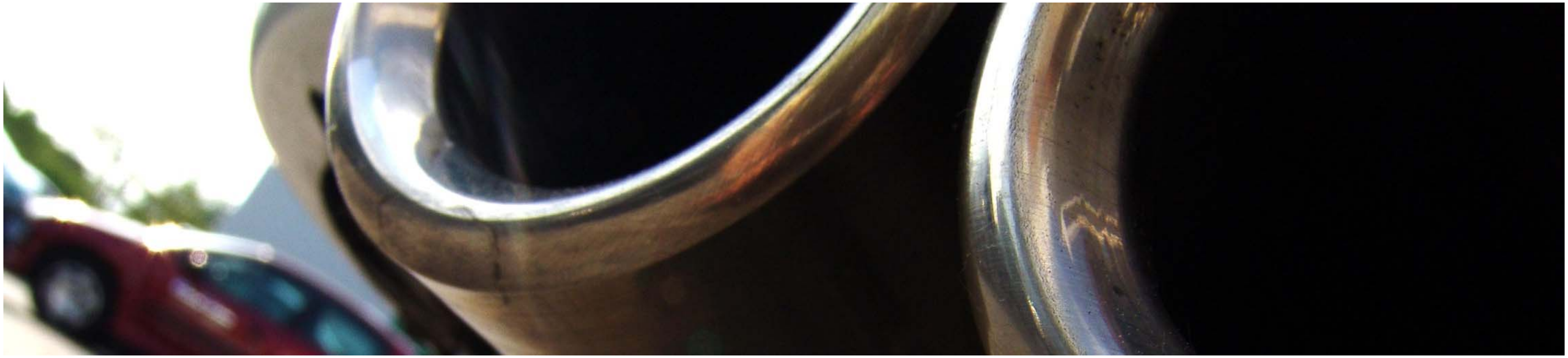
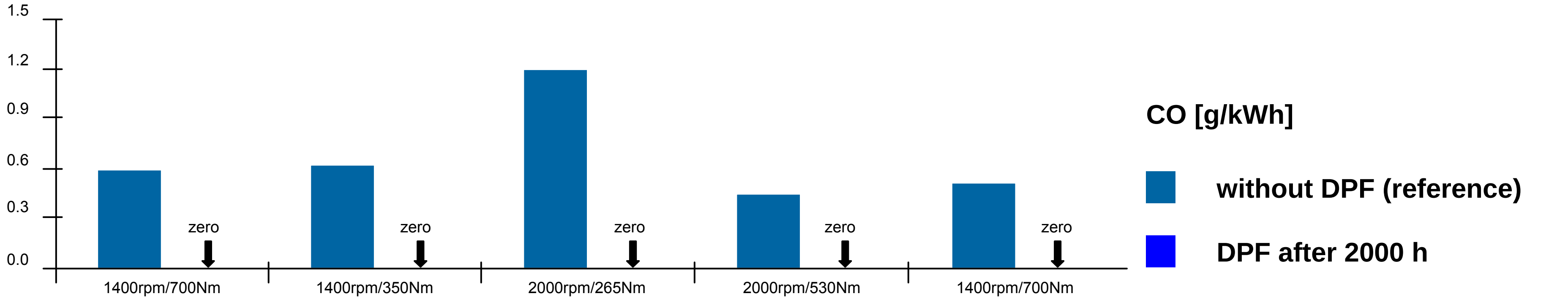




engine: Liebherr D 934 S A6;
fuel: ulsd (S<10 ppm)

Can we detect and quantify such low levels of Pt emmisions?

12

Quantifying the emission of Pt in real life

Messung TÜV Hessen Motorprüfstand

Pt/Ce FBC mass balance theoretical

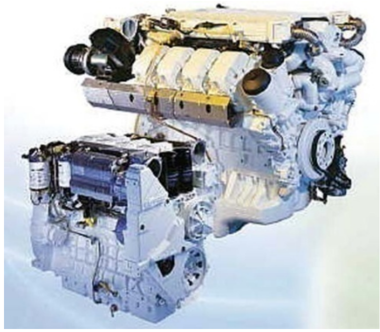
ETC-Test	TÜV Hessen	
Dosierrate Platin (TÜV)	0.3	mg/kg Kraftstoff
Dosierrate Cer (TÜV)	7.5	mg/kg Kraftstoff
Abscheiderate Platin Motor (VSET)	97.90%	%
Abscheiderate Cer Motor (VSET)	92.20%	%
Abscheiderate Platin DPF (VSET)	92.80%	%
Abscheiderate Cer DPF (VSET)	94%	%
Abscheiderate Partikel DPF Daugbjerg (TÜV)	96.60%	%
Dauer	30	min
Kraftstoffverbrauch pro ETC	7.45	kg
Motorleistung im ETC	63	kw
Partikelemission vor Filter (TÜV)	0.171	g/kWh
Partikelemission nach Filter (TÜV)	0.0053	g/kWh
Platinzufuhr in den Motor	2.235	mg
Cerzufuhr in den Motor	55.875	mg
Platin vor Filter	0.0469	mg
Cer vor Filter	4.3583	mg
Partikel vor Filter	5387	mg
Platin nach Filter	0.0034	mg
Cer nach Filter	0.2615	mg
Partikel nach Filter	183	mg

Massenbilanz pro km Fahrleistung

Abscheiderate Platin Gesamt: Motor und Filter
Σ 99,85 % (nach VSET)

Zufuhr

41,67µg/km Pt
1041,75 µg/km Ce



Motor aus

875 ng/km Pt
81,26 µg/km Ce

nach DPF

63 ng/km Pt
4,87 µg/km Ce

Abscheideraten Motor:
- Pt: 97,9% (VSET)
- Cer: 92,2% (VSET)

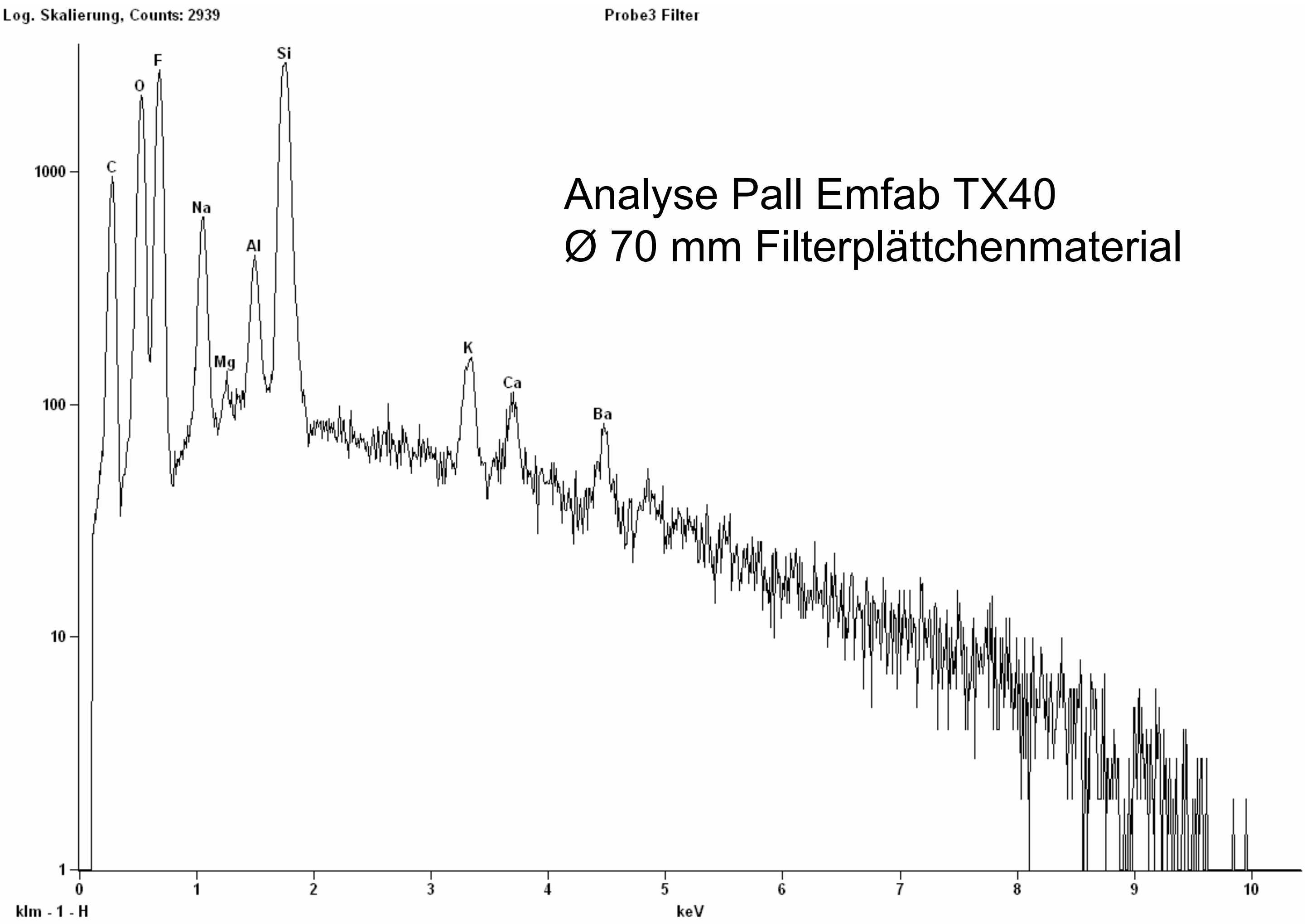
Abscheideraten DPF:
- Pt: 92,8% (VSET)
- Cer: 94% (VSET)

Additivdosierung:	1:3000
Pt - Dosierung [mg/kg Kraftstoff] :	0,3
Ce - Dosierung [mg/kg Kraftstoff] :	7,5

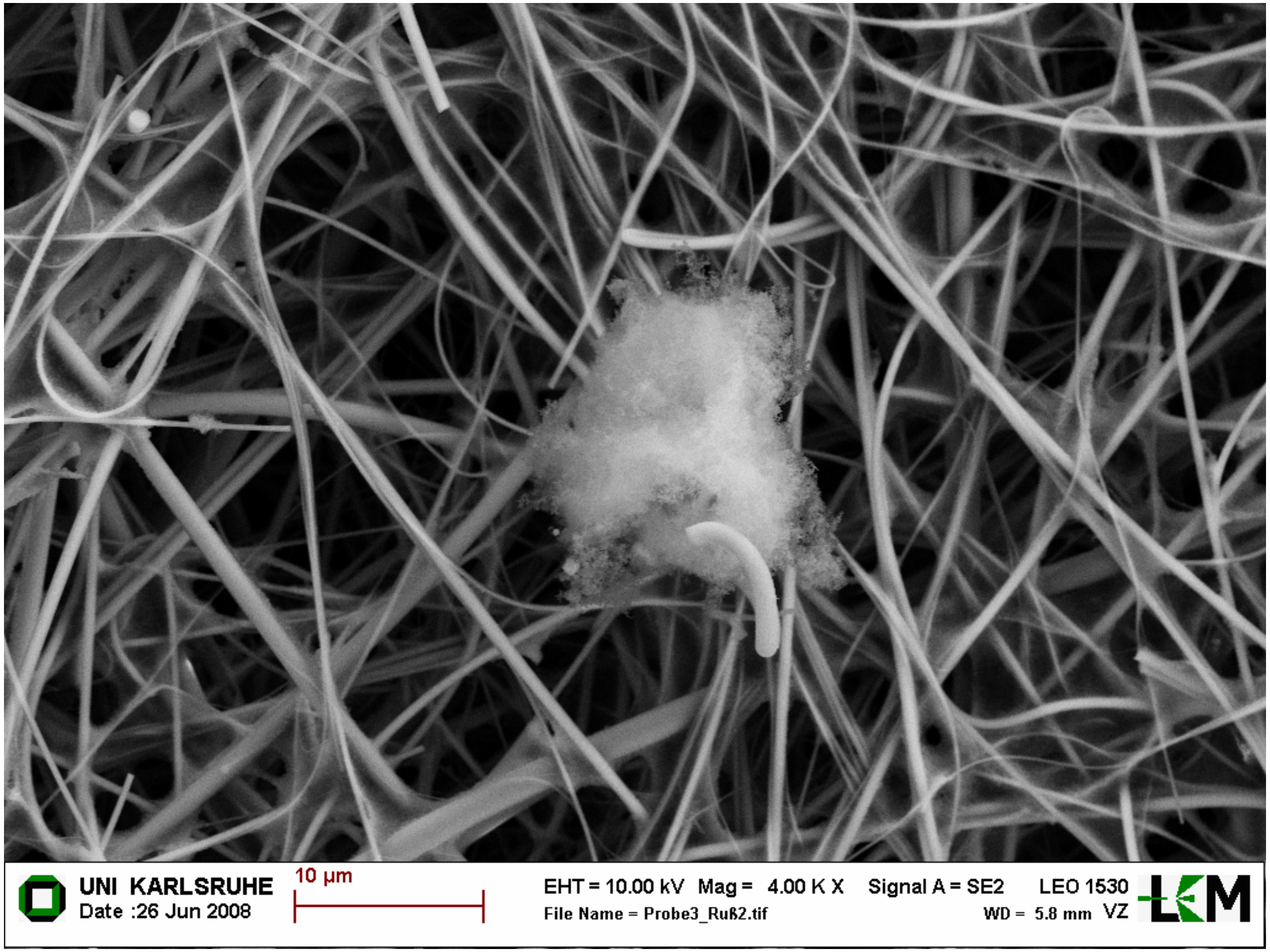
Scanning Electron Microscope(SEM)

- Universität Karlsruhe Lab for Electron Microscope
- Scanning Electron Microscope(SEM)
- Type: „Gemini Leo 1530“
- Particle filter pads were examined from the engine test bench with the engine running in ETC test cycles
- Cycle:
- **Probe 1: Serial with additive ETC no DPF (15.04.08)**
- **Probe 2: Serial ETC (18.03.08)**
- **Probe 3: ETC with DPF & FBC after 17 cycles (09.04.08)**

Probe 3 – Reference



Probe 3 – With FBC with DPF



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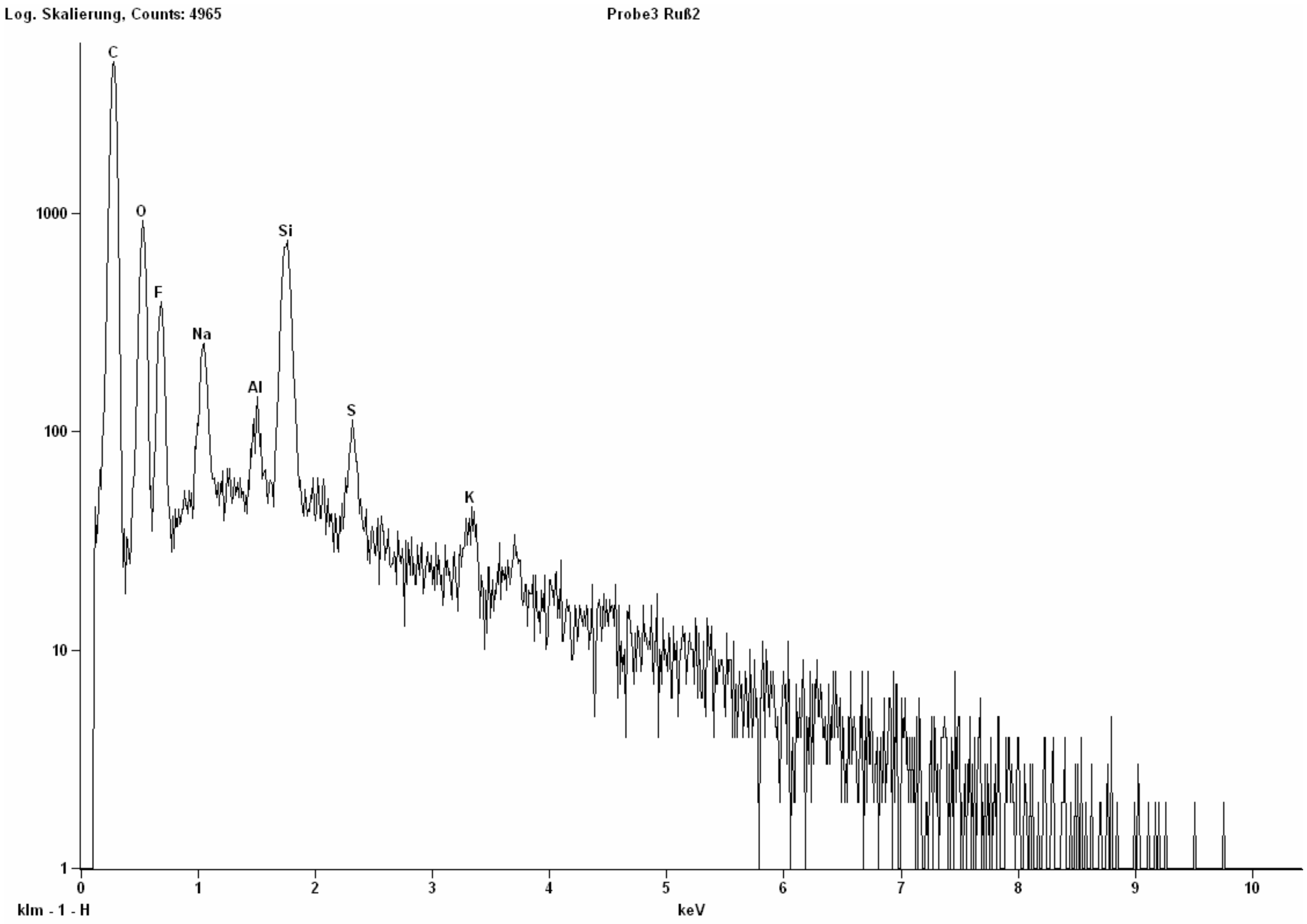

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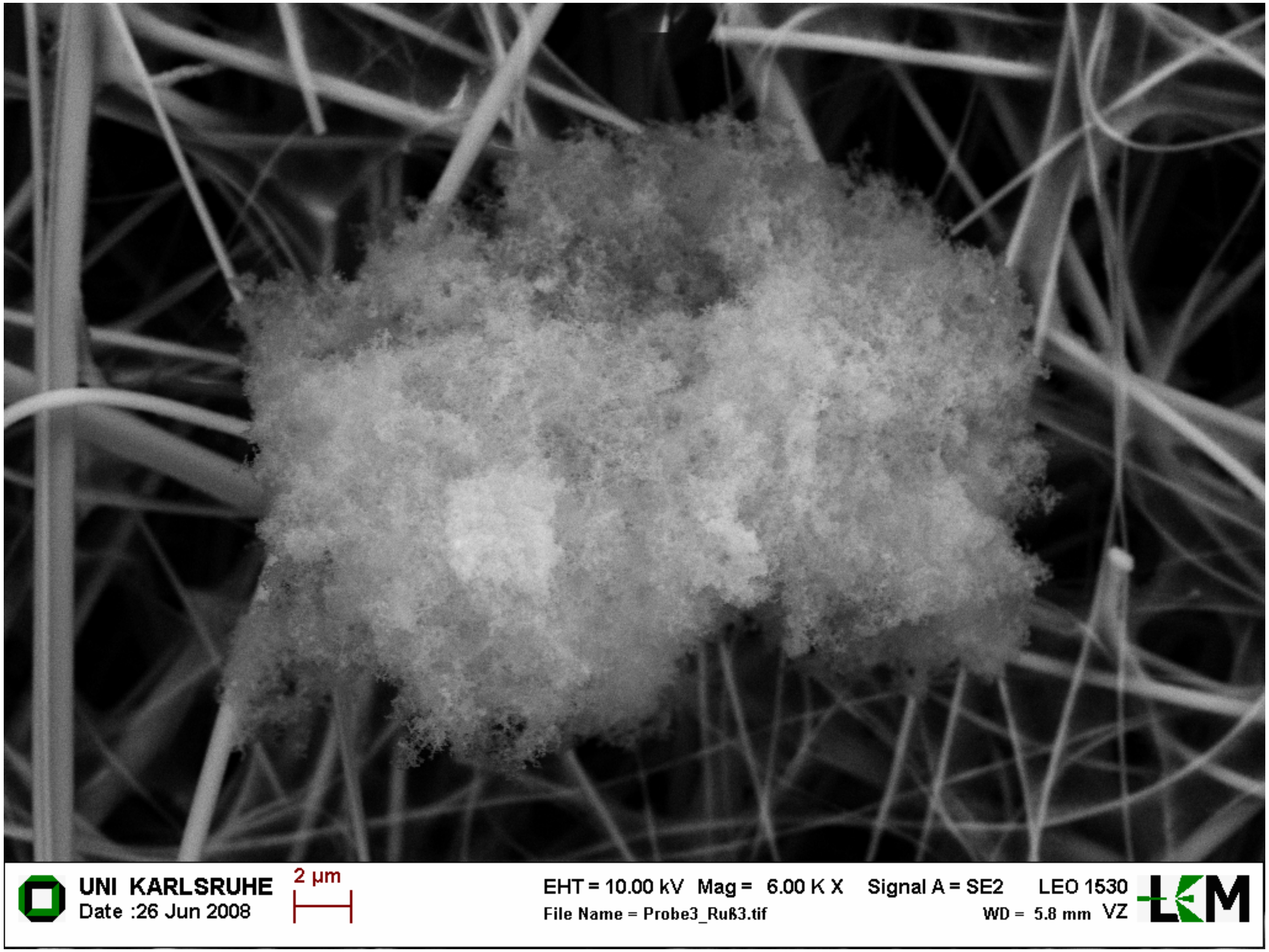

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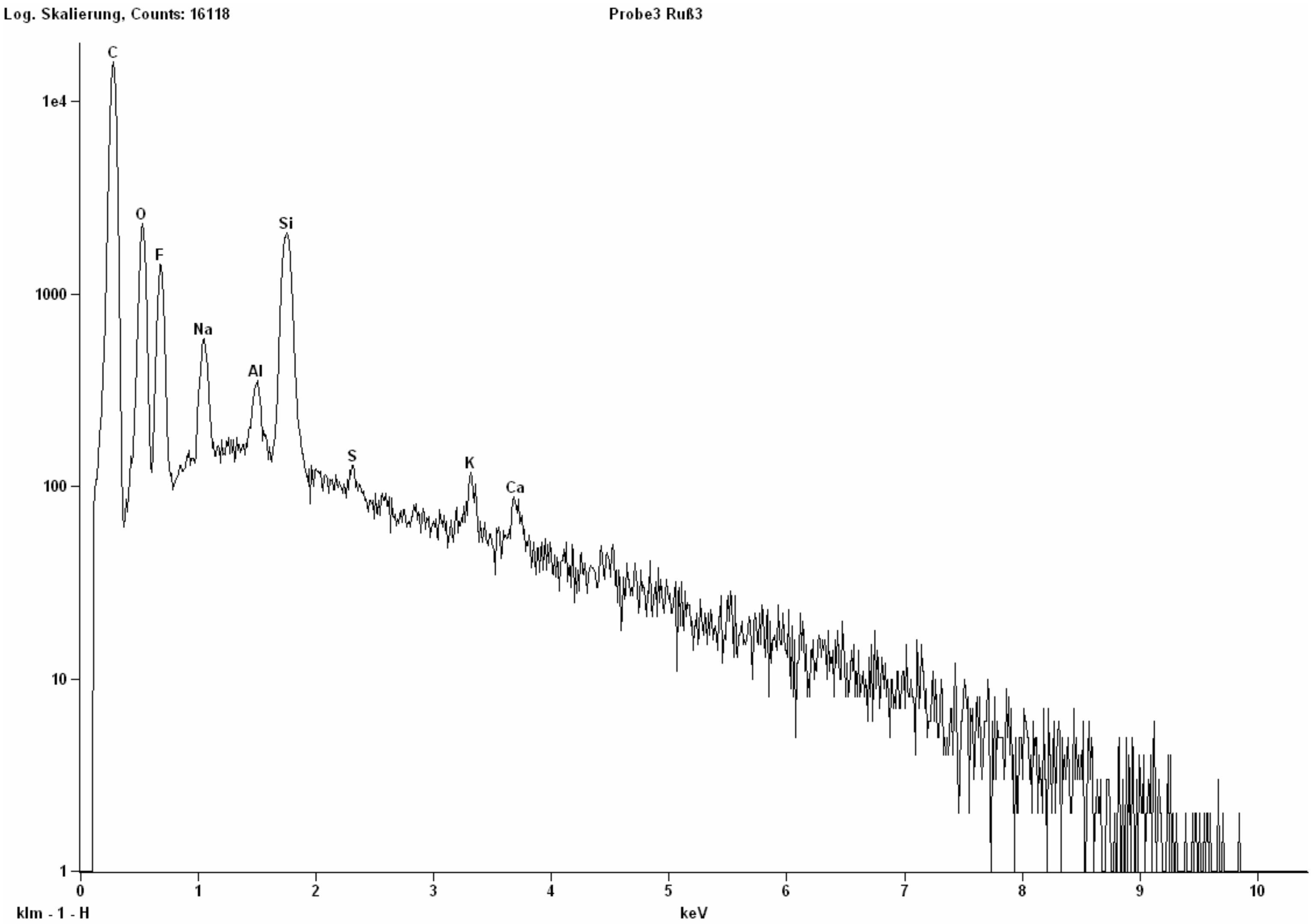

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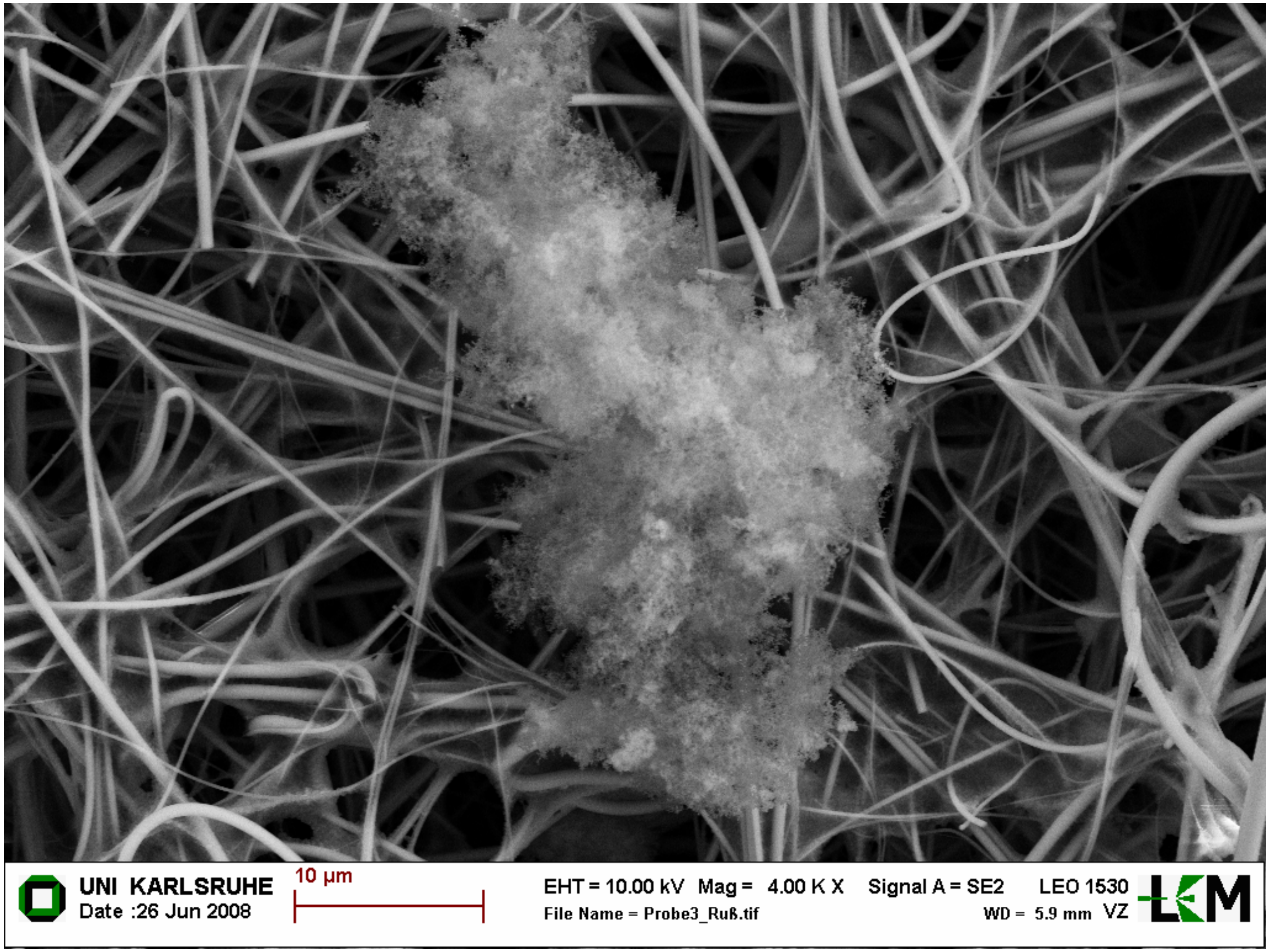

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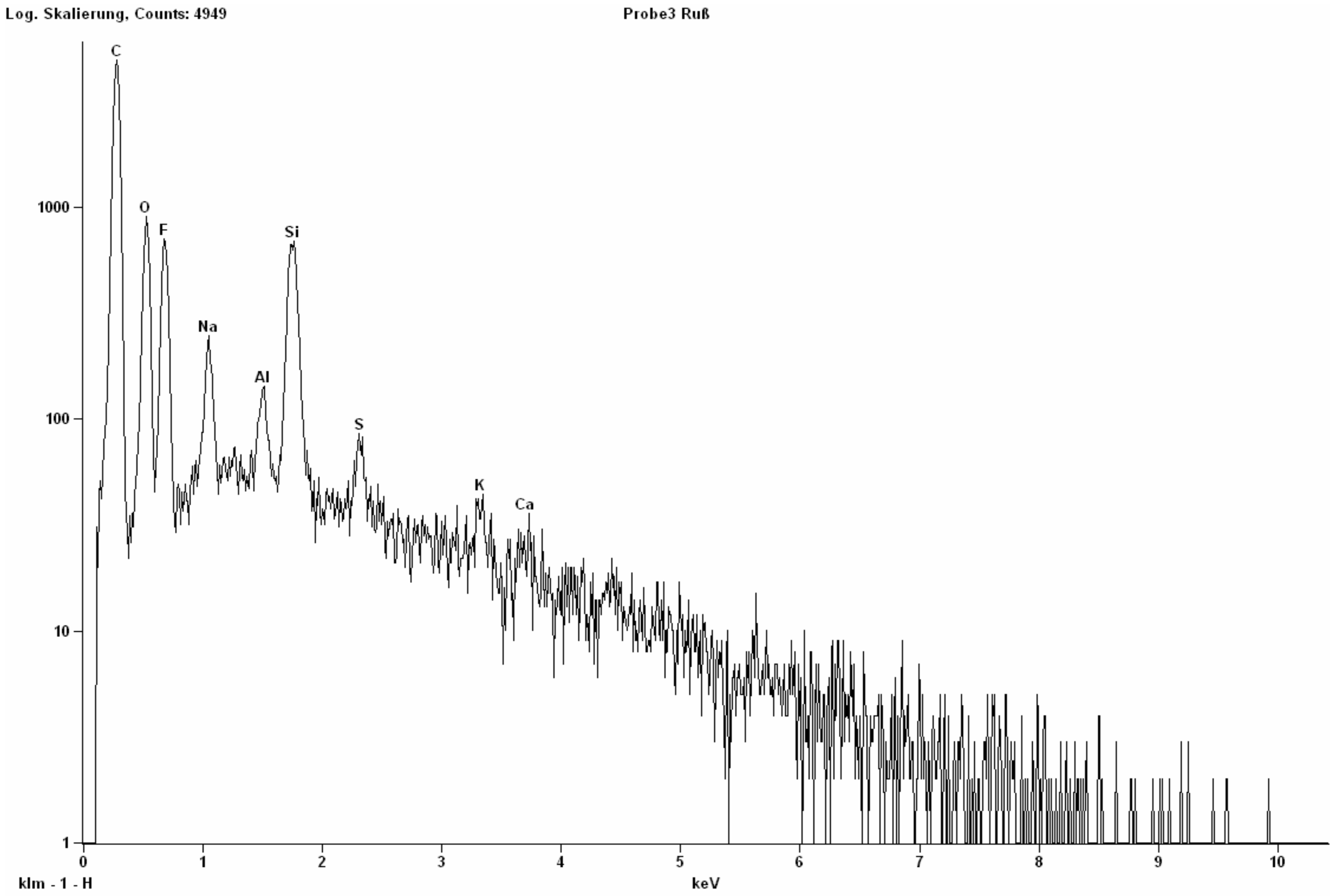
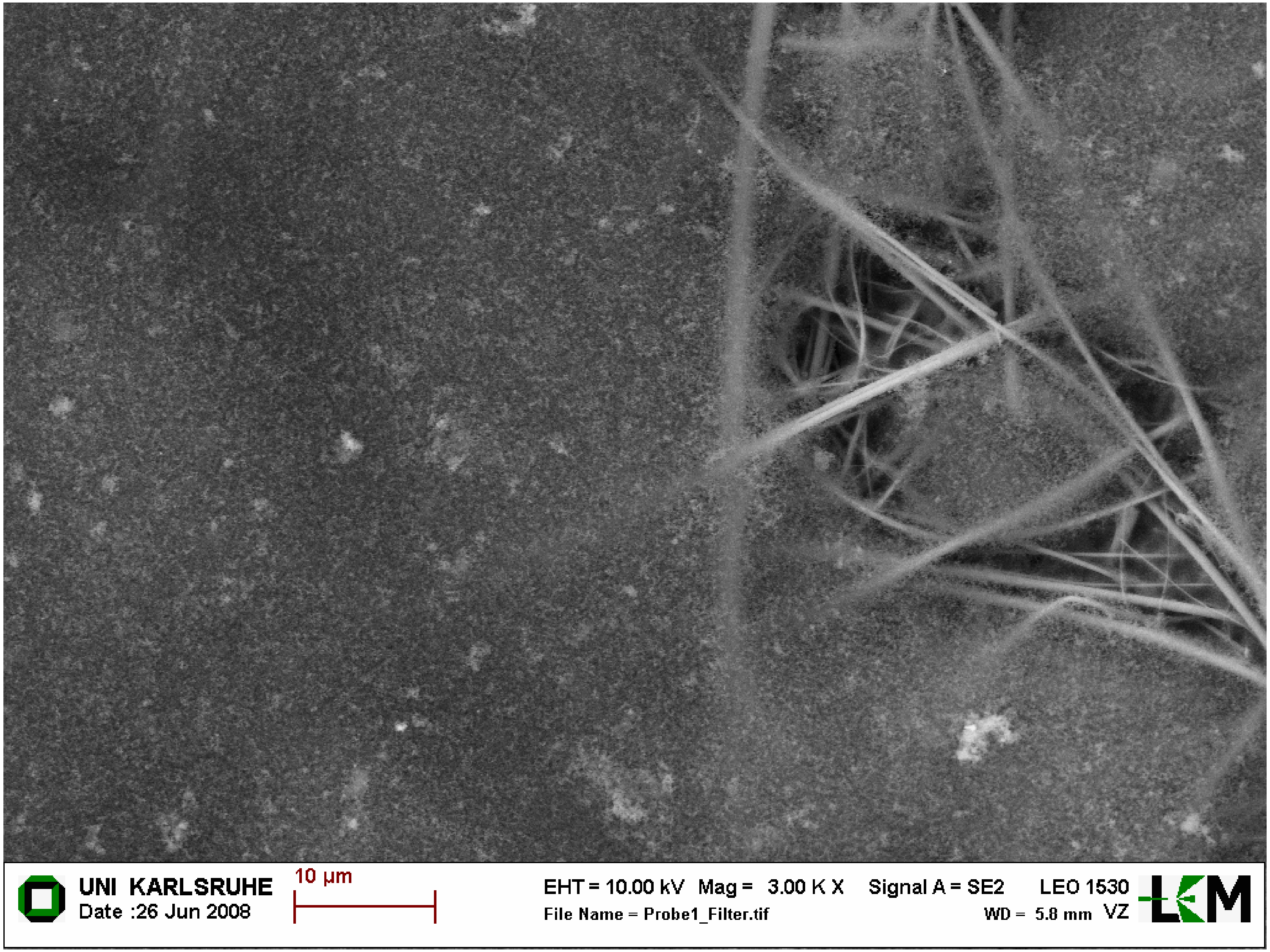


Probe 1 – With FBC no DPF



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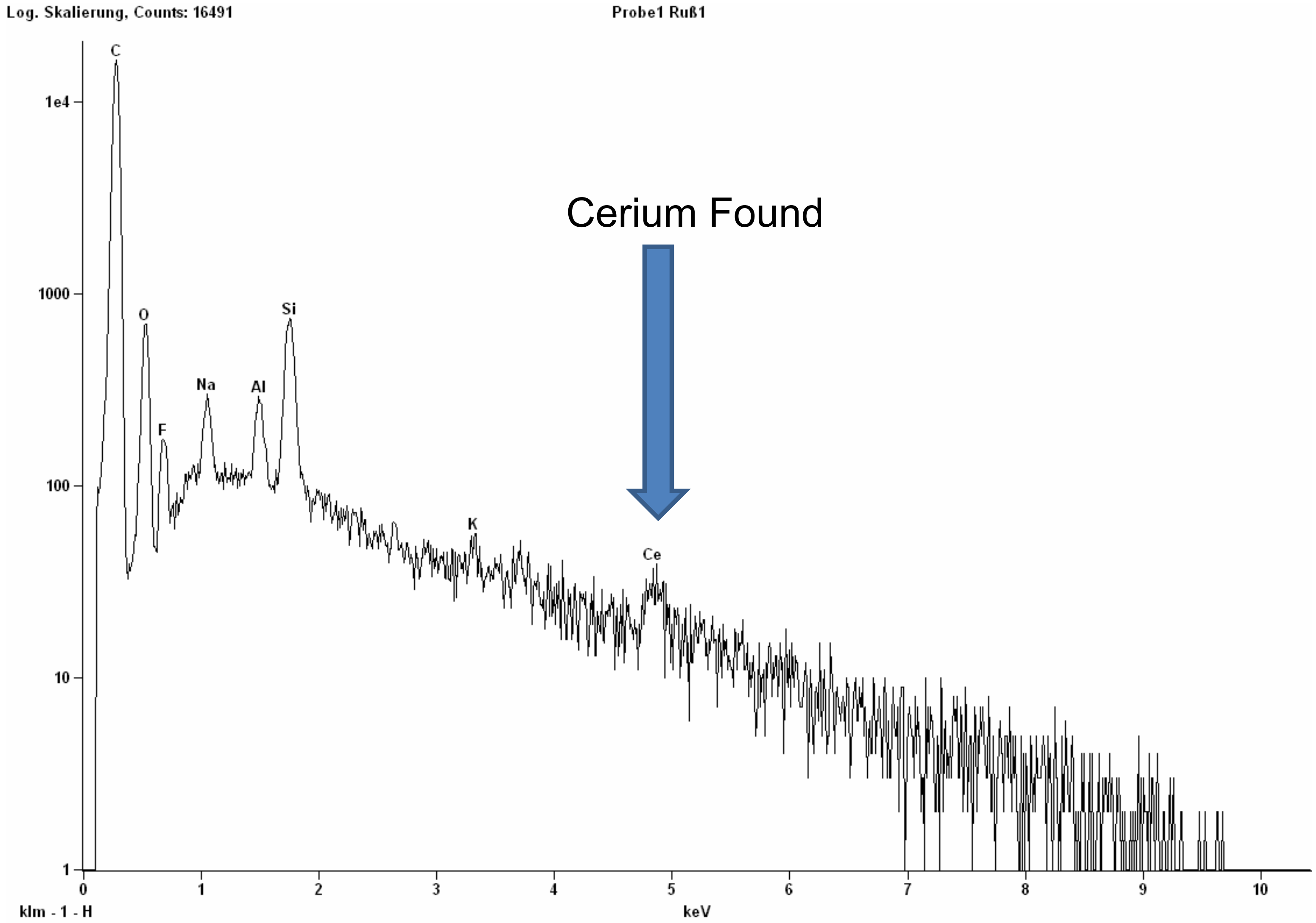

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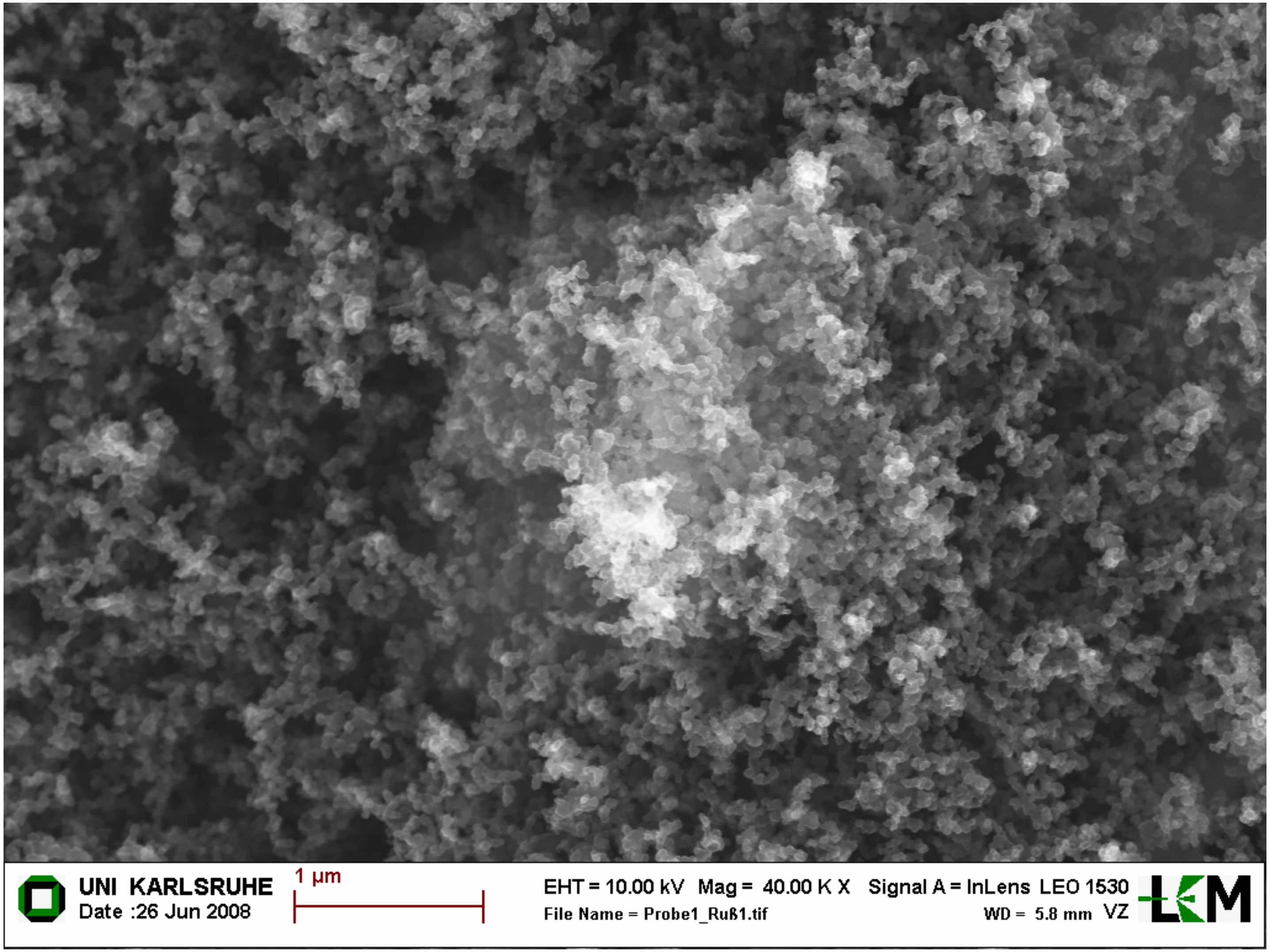

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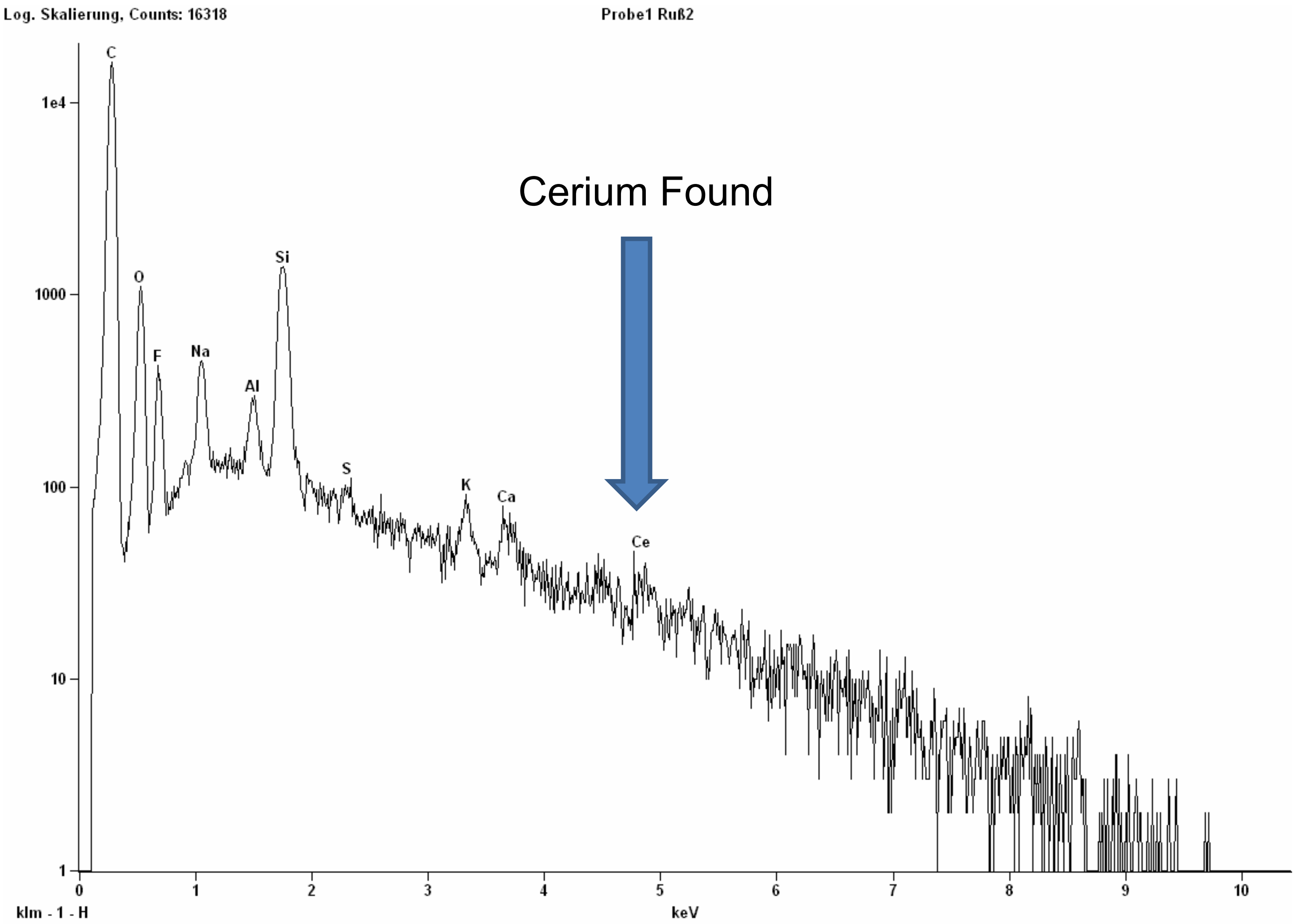

AAS-Analysis of the Filter Ash

Atomic Absorption Spectrometry (AAS)

- Location: Universität Karlsruhe, Institut für Technische Chemie und Polymerchemie, Kaiserstr. 15, 76131 Karlsruhe
- Measuring equipment : Spectrometer, Type Hitachi Z-6100
- Procedure: After finishing the engine bench tests 20 ETC cycles, 2,53 g of particles were taken out from DPF , engine side. Conditioning in a furnace the particle mass was reduced to 1,2 g by incineration/ashing. This solid remainder was dissolved in nitrohydrochloric acid and this dilution was analysed using the AAS.
- Result of the probe: The amount of Platinum found in the filter ash was

  1,3 mg Platinum/g Particle. This compared to a calculated value of 0.9 mg Pt/g
- **TUV Hessen Assessment:**
  The measured particle concentration reflects a very effective ability of retention of the Liqtech substrate as well as the effect of concentration of Platinum by soot particle regeneration.

South West Research Institute (SwRI).

Aerosol sampling was performed in a test cell at the South West Research Institute (SwRI). The engine used was a Cummins N-14 diesel engine running on ultra-low sulfur diesel fuel (ULSD). The sequence of engine validation/operation/sampling for this program is outlined below:

- Power validated on untreated No. 2 LSD Reference fuel.
- Baseline cold and triple hot start FTP cycle run using No. 2 LSD fuel. [*PM collected using both 90mm and 47mm filter trains*]
- Repetitive FTP cycles run for 2 hours with ULSD to purge engine.
- ULSD baseline cold and triple hot start FTP cycle run. [*PM collected using both 90mm and 47mm filter trains*].
- Engine run for 25 hours using Cummins DURABILITY cycle using ULSD amended with bimetallic FBC-DFX (0.15 ppm Pt + 7.5 ppm Ce).
- A cold and triple hot start FTP cycle was run using FBC-DFX amended ULSD [***PM collected using both 90mm and 47mm filter trains***].
- A second cold and triple hot start FTP cycle was run using FBC-DFX amended ULSD [***PM collected using both 90mm and 47mm filter trains***].
- A CAS DPF (diesel particulate filter) was installed on the engine exhaust. The DPF was regenerated/conditioned for 2 hours with the engine running ULSD amended with 0.5 ppm Pt + 7.5 ppm Ce (DFX-DPF) over Cummins DURABILITY cycle. Repetitive FTP cycles were then run for a period of 4 hours to load the DPF.
- A cold and triple hot start FTP cycle was run using DFX-DPF amended ULSD [***PM collected using both 90mm and 47mm filter trains***].

- From filter-borne samples of aerosol particulate matter derived from combustion of platinum+cerium amended diesel fuel determine the concentrations of:
-
- **Total** platinum, cerium, and ancillary (iron, sulfur) elements
- **Water-soluble** platinum, cerium, and ancillary elements
- **Methanol and dichloromethane-soluble** platinum, cerium and iron
- **Colloidal and Dissolved** platinum, cerium, and iron in aqueous **and** organic solvent extracts of filters
- **Anionic and Non-Anionic** fractions of platinum and cerium in filtered aqueous **and** solvent extracts
- **Parent FBC** (diphenyl(1,5-cycloocatadiene)platinum(II) in solvent extracts
-

Speciation of Pt emissions

ELEMENTAL QUANTIFICATION

- The concentrations of platinum (Pt) and cerium (Ce) were determined in each sample/fraction by high-resolution inductively-coupled plasma mass spectrometry (HR-ICP-MS). A Finnigan Element 2 HR-ICP-MS with fast scanning magnet, interfaced to an ESI low-flow (80 µL min-1) Teflon micro-concentric nebulizer was used. The complete analytical system is located within a trace metal clean room. Platinum was quantified in both medium (4500) and low (400) resolution using m/z 194.965 (195). The other two major Pt isotopes (194 and 196) were also acquired as standard quality assurance practice.

Result summary

FTP Cycle (Cold and average of all Hot Cycles) and Treatment (with and without a Diesel Particulate Filter (DPF) means of Total Metals **All ng/filter.**

Metal	Cold (n=3)		Hot (n=9)		DPF-Cold (n=2)		DPF-Hot (n=2)	
	Mean	**±**	**Mean**	**±**	**Mean**	**±**	**Mean**	**±**
Pt	364	53	85.2	18.7	2.1	1.2	1.2	0.2
Ce	6260		7030	540	4.6	0.7	2.3	0.1
Fe	2120	1030	1470	830	1870	1770	2870	3760
S	2040	820	790	220	371	64	397	12

Comparative Platinum Emission Ra

	Pt emissions, ug/mi	Data Comments
Three-way Monolith (Light Duty)	<D.L. 0.003 – 0.22 0.02 & 0.16	3 dyno studies 6 dyno studies PM2.5 & PM10 Schauer tunnel study
Diesel Oxidation Catalyst (LD)	0.05 - 1.3	2 dyno studies
Fuel-borne Catalyst, Platinum Plus Medium Duty FBC-DPF	0.28-2.6	Based on 2 dynamometer tests at commercial doses of 0.3 ppm Pt ppm 7.5 Ce