

Sedimentation field flow fractionation (SdFFF) of soot particles emitted by a light duty diesel

James R. Kassab^{1,2}, Annett Wollmann³, Richard Zahoransky²,
Michael Claussen³, Philippe J.P. Cardot^{1*}

1 Laboratoire de Chimie Analytique et de Bromatologie, Université de Limoges Faculté de Pharmacie, 2 Rue du Dr. Marcland, F-87025 Limoges

2 Fachhochschule Offenburg, University of Applied Sciences, Badstr. 24, D-77652 Offenburg

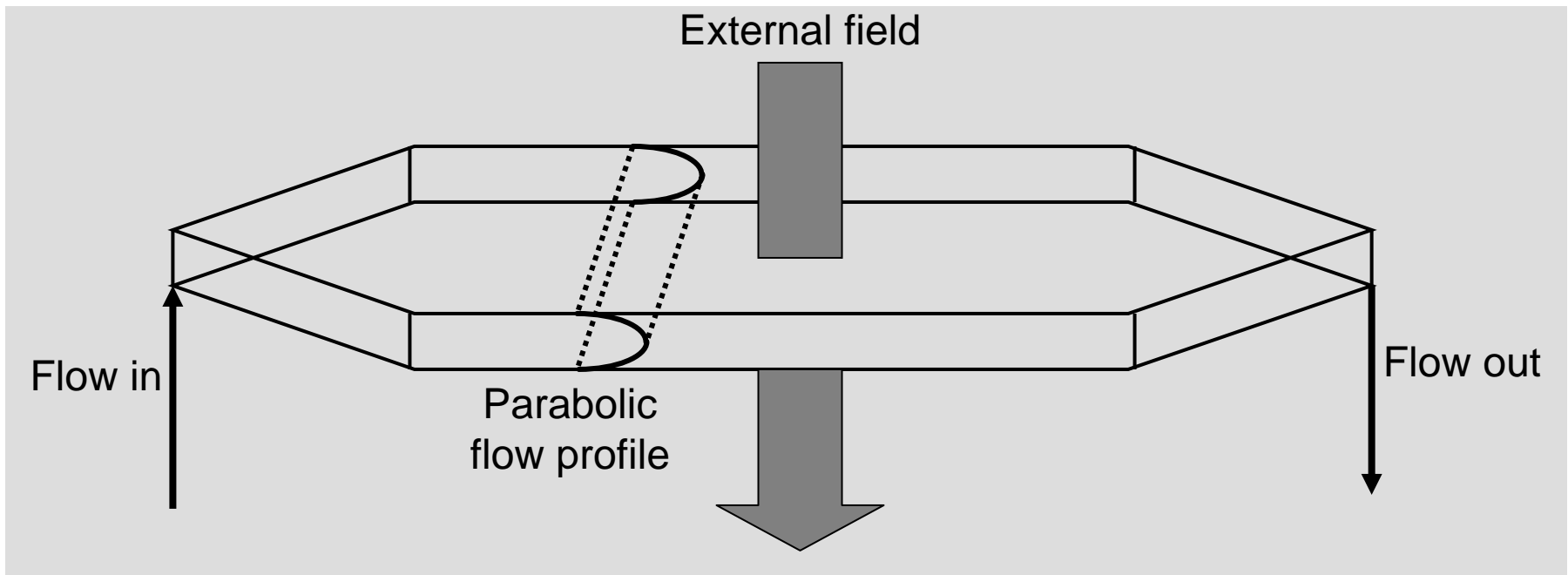
3 CUTEC Institut GmbH, Leibnizstr. 21 & 23, D-38678 Clausthal-Zellerfeld

Content

- Field Flow Fractionation: Subtechnique Sedimentation FFF SdFFF; theory of retention and field programming
- Off-line hyphenation of SdFFF with Optical Multiwavelength Technique (OMT) for particle analysis
- SdFFF system in use
- Soot collection and sample preparation
- Soot fractionation and size analysis by OMT
- Comparison to size analysis by SMPS
- Conclusion

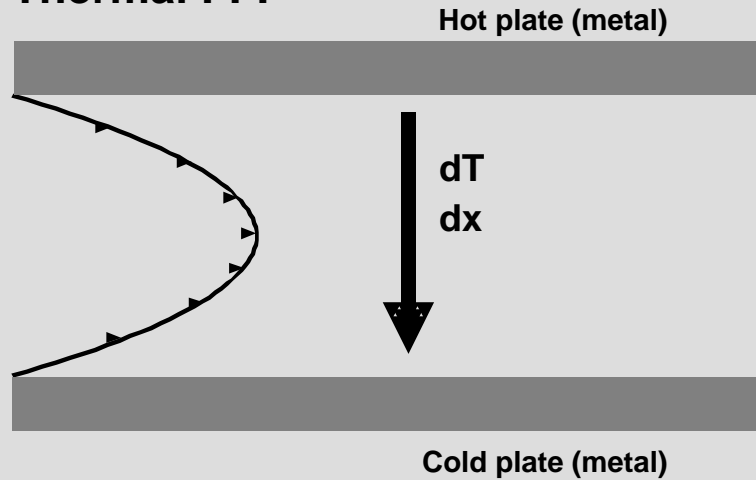
Field Flow Fractionation (FFF)

- First conceptualized by Giddings 1960s
- Separation occurs inside a thin ribbonlike channel clamped between two highly polished plane and parallel walls

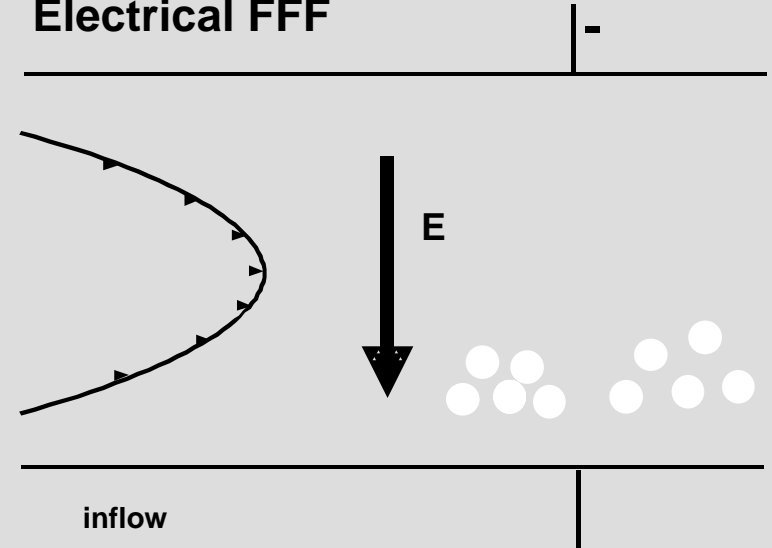


Overview on FFF subtechniques

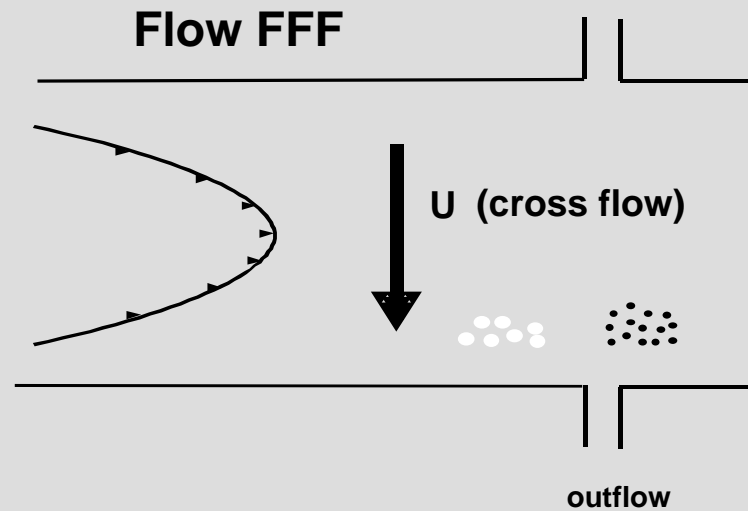
Thermal FFF



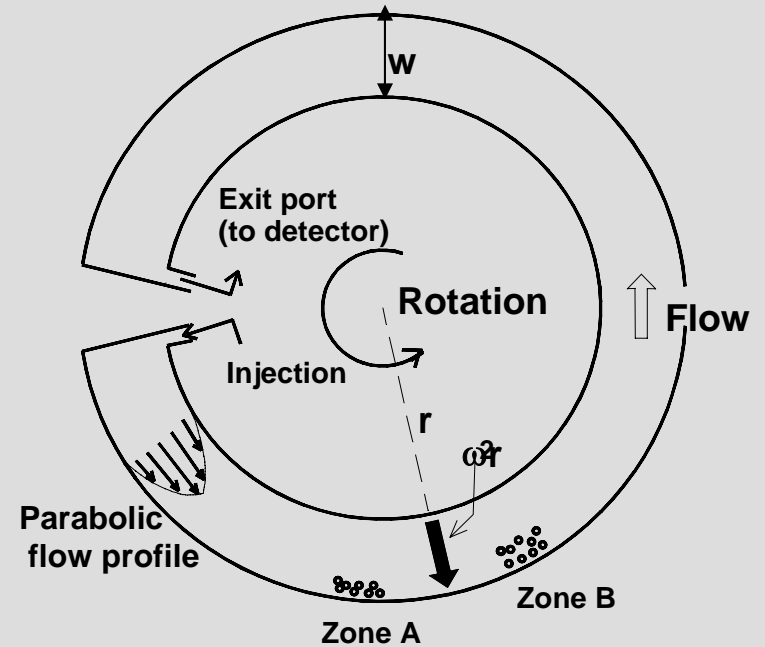
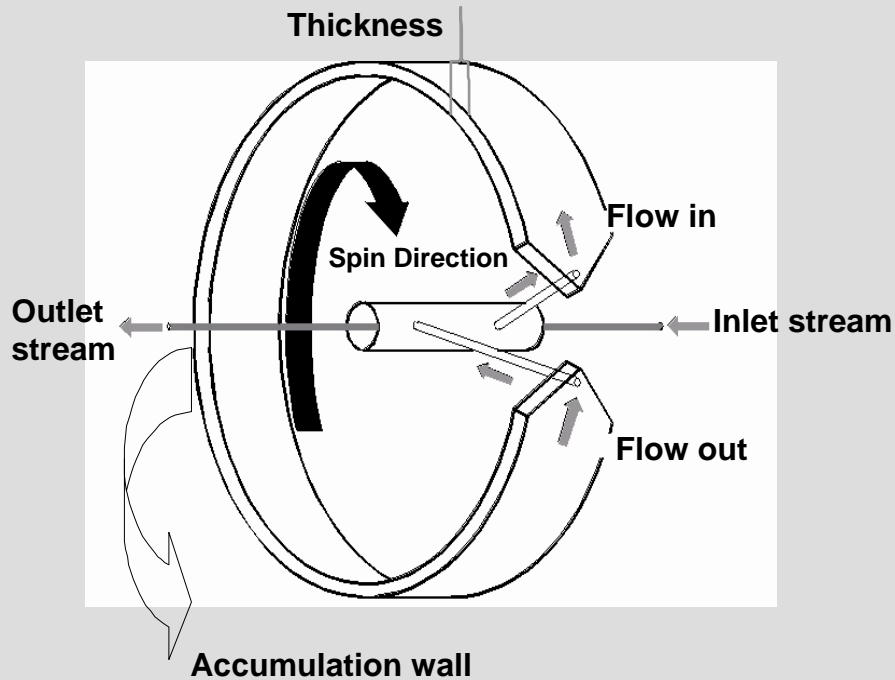
Electrical FFF



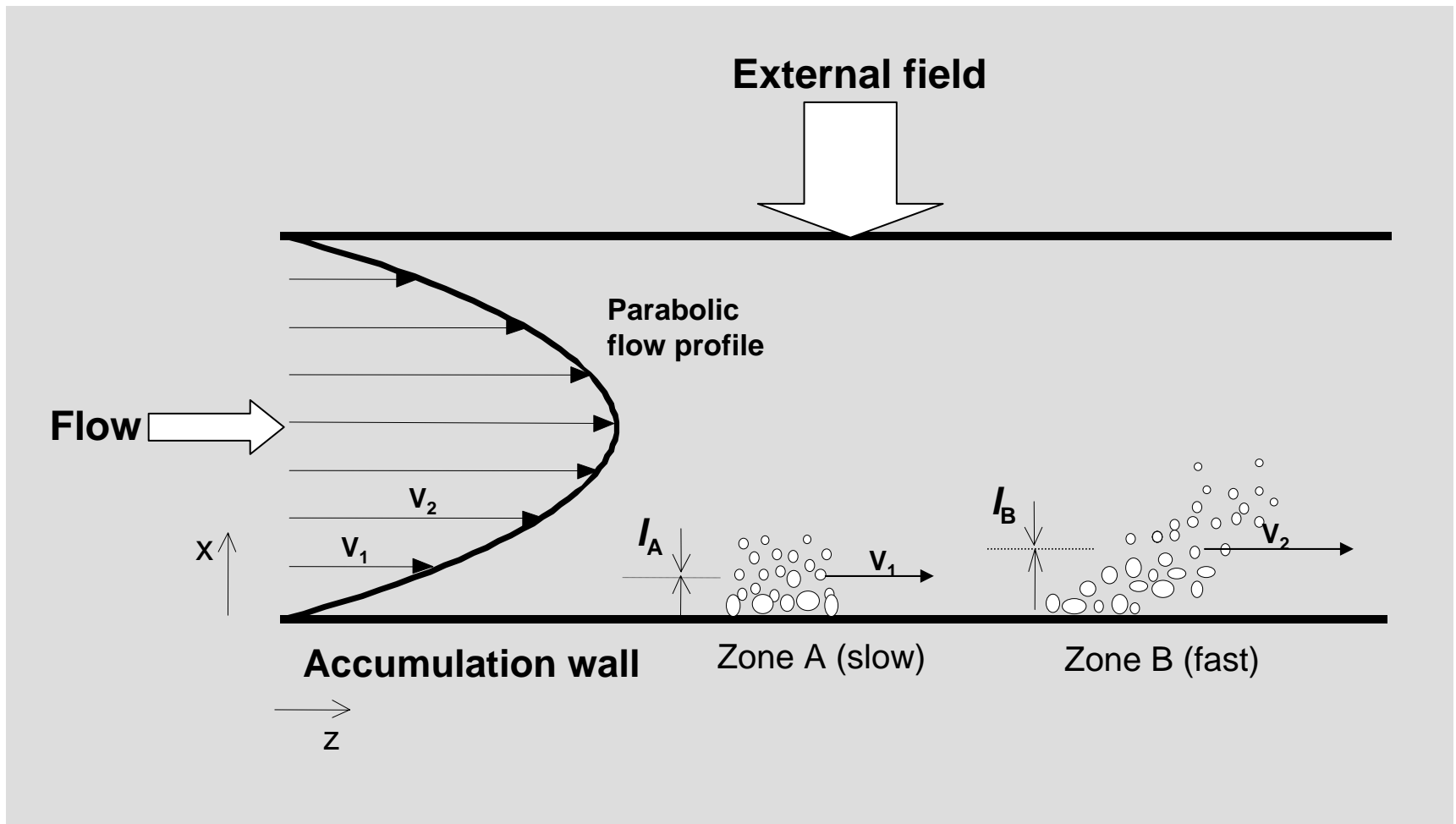
Flow FFF



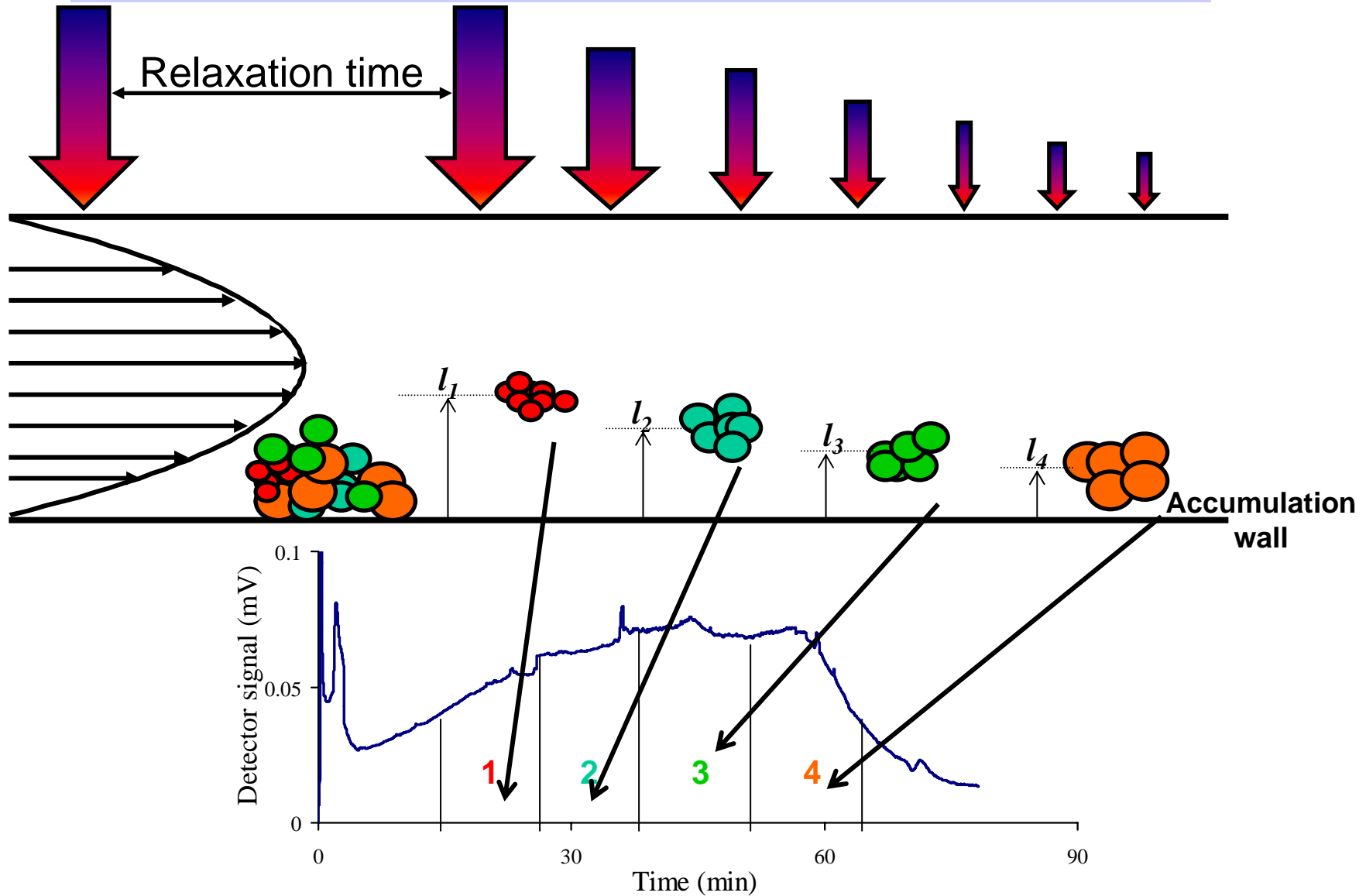
Sedimentation FFF (SdFFF)



Retention in the normal mode



Sedimentation field programming



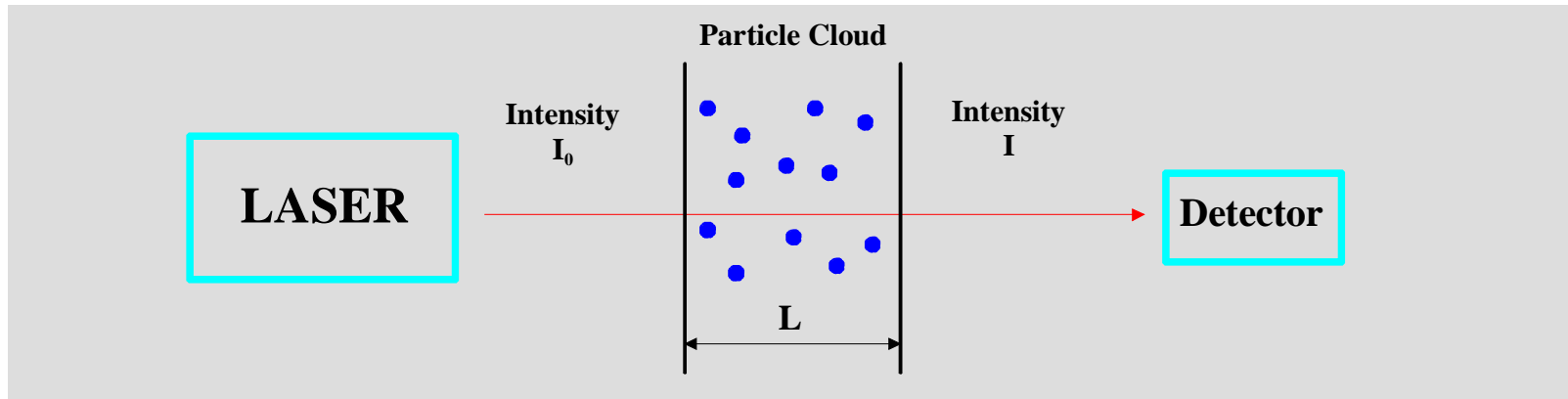
Off-line hyphenation of OMT with SdFFF

Combining the size separation technique SdFFF with the particle sensor

OMT (Optical Multiwavelength Technique WIZARD DQ):

- Benefit from the separation potential of SdFFF to measure the mean particle sizes of collected fractions obtained from broadly distributed particulate sample
- Confirmation whether a selective FFF separation occurred according to the concerned elution mode
- Obtained sizes can be compared to those determined by other sizing techniques such as EM and PCS

Dispersion Quotient Technique (1): OMT principle



monodisperse

$$I = I_0 \cdot \exp\{-N \cdot L \cdot \pi \cdot r^2 \cdot Q_{\text{ext}}(r, \lambda, n)\}$$

polydisperse

$$I = I_0 \cdot \exp\{-L \cdot N \cdot \pi \cdot \int r^2 \cdot Q_{\text{ext}}(\lambda, r, n) \cdot p(r) dr\}$$

with:

I = intensity

I_0 = initial intensity

N = particle concentration

L = optical path length

r = particle radius

Q_{ext} = extinction coefficient

λ = wavelength

n = refractive index

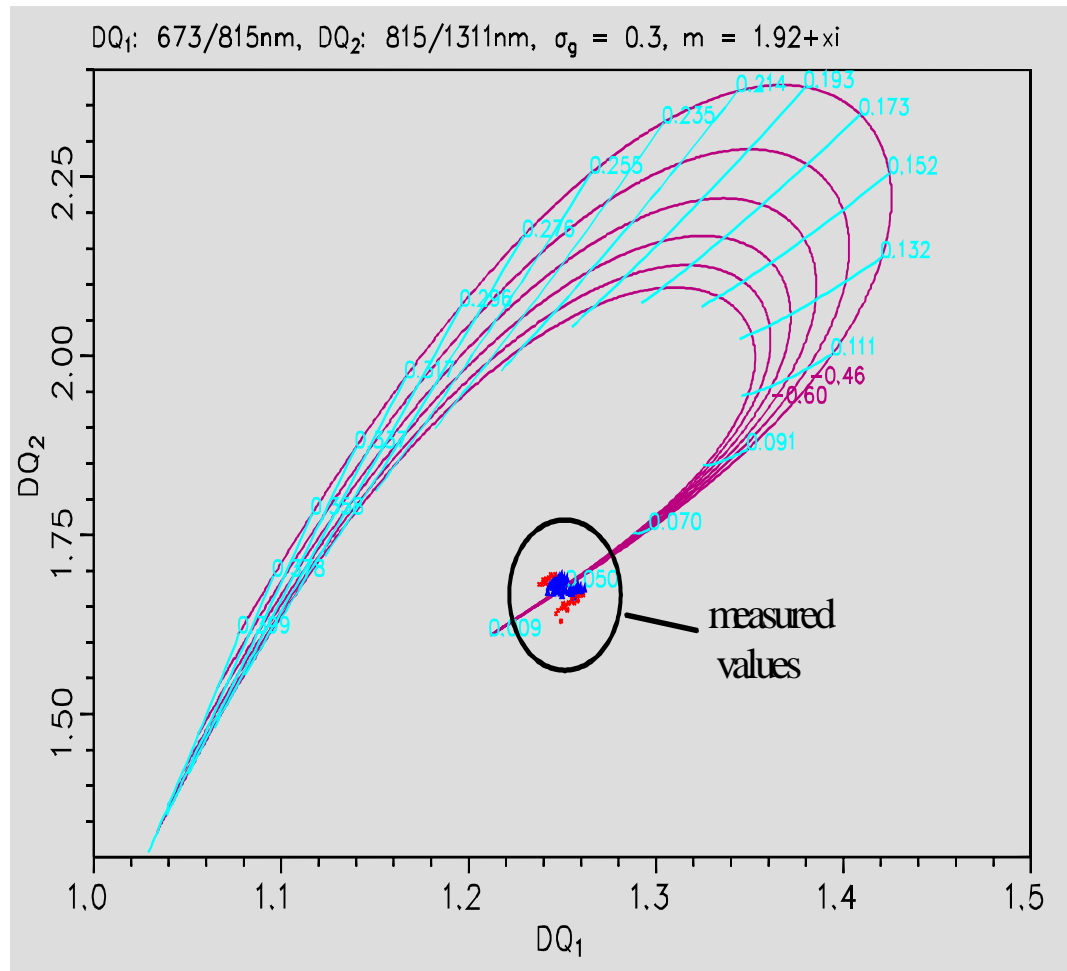
$p(r)$ = number distribution

Dispersion Quotient Technique (2)

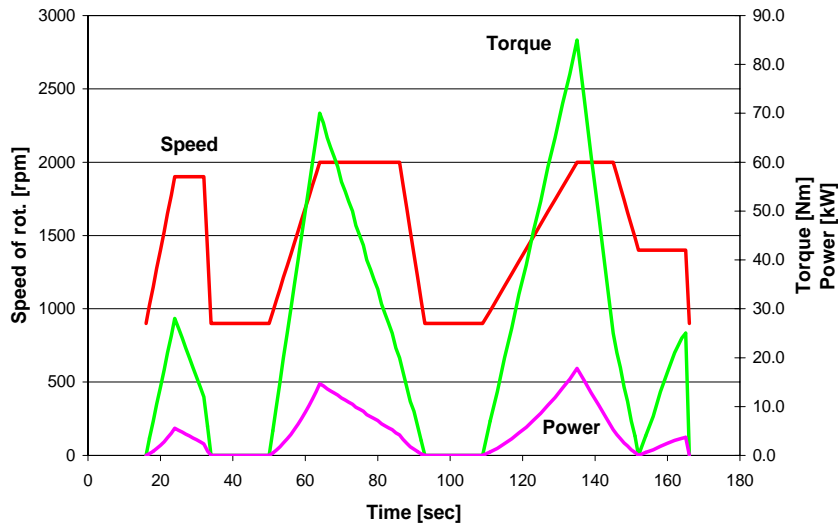
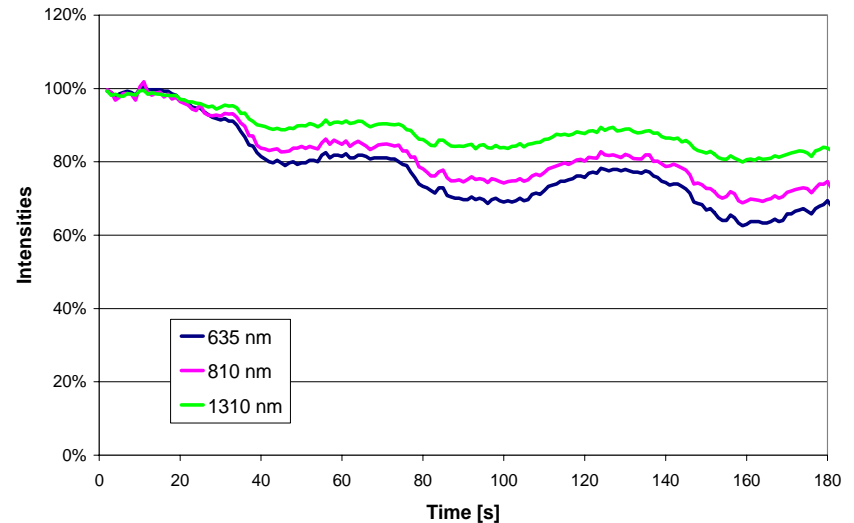
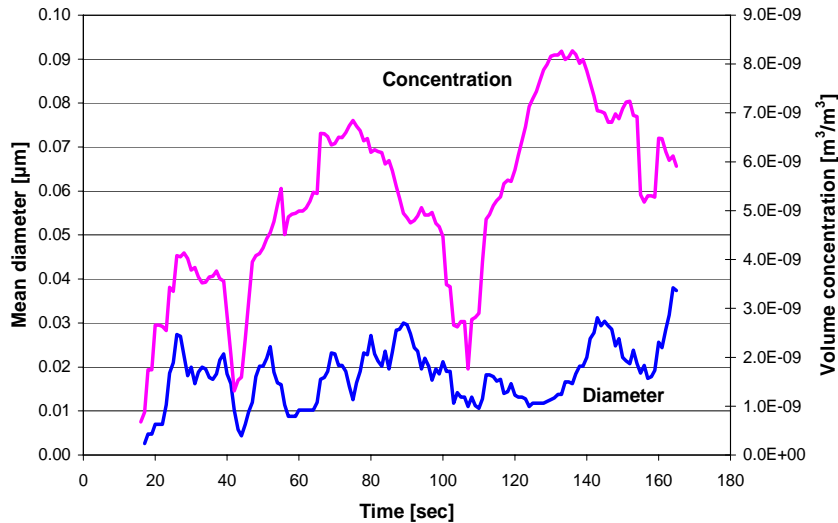
OMT Principle

$$DQ_1 = \frac{\ln\left(\frac{I}{I_0}\right)_{\lambda_1}}{\ln\left(\frac{I}{I_0}\right)_{\lambda_2}}$$

$$= \frac{-N \cdot L \cdot \pi \cdot r^2}{-N \cdot L \cdot \pi \cdot r^2} \cdot \frac{Q_{ext}(r, \lambda_1, n)}{Q_{ext}(r, \lambda_2, n)}$$



Transient Measurements (ECE)

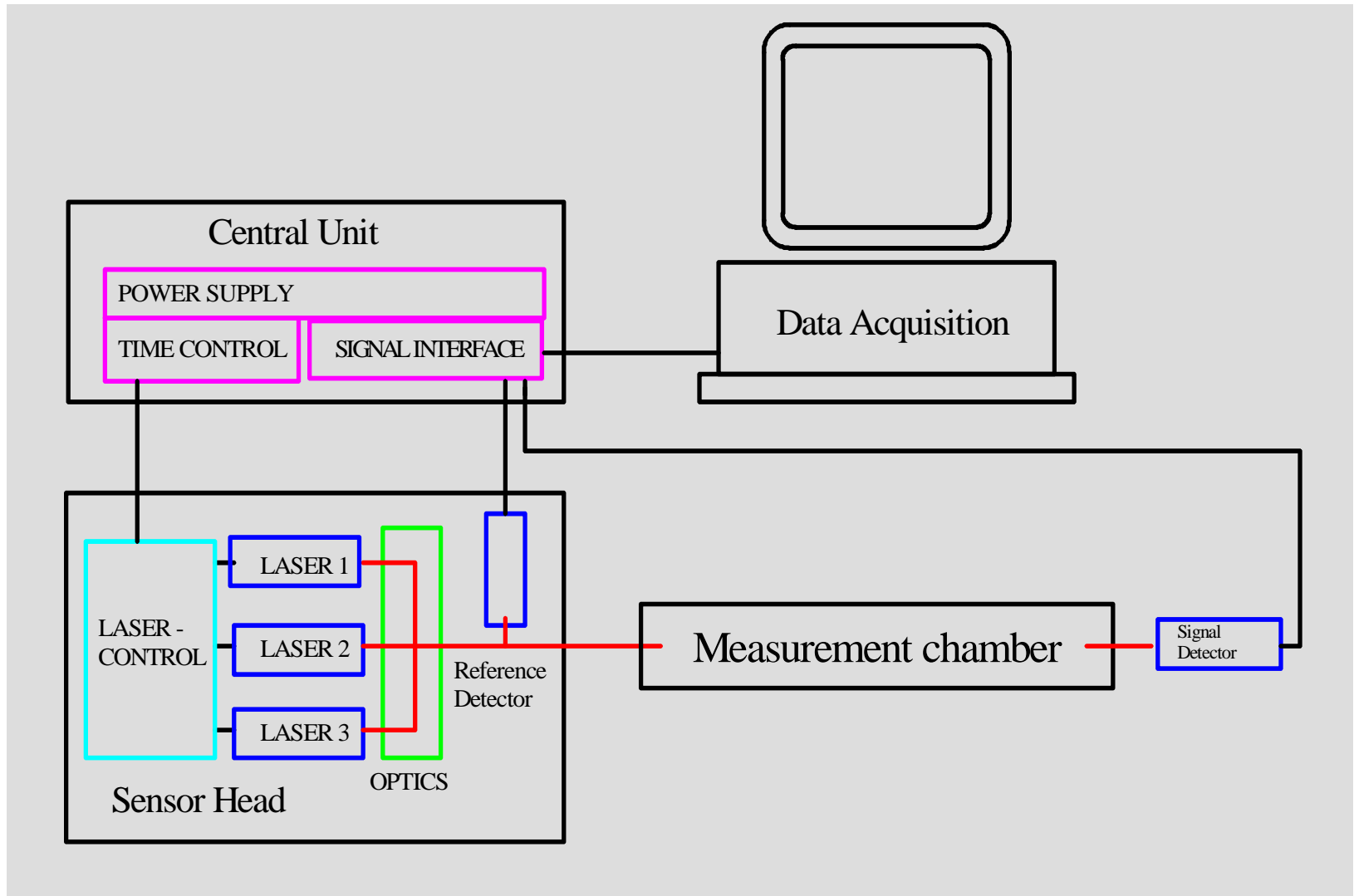


**OMT Particle Analyzer
(WIZARD-DQL)**

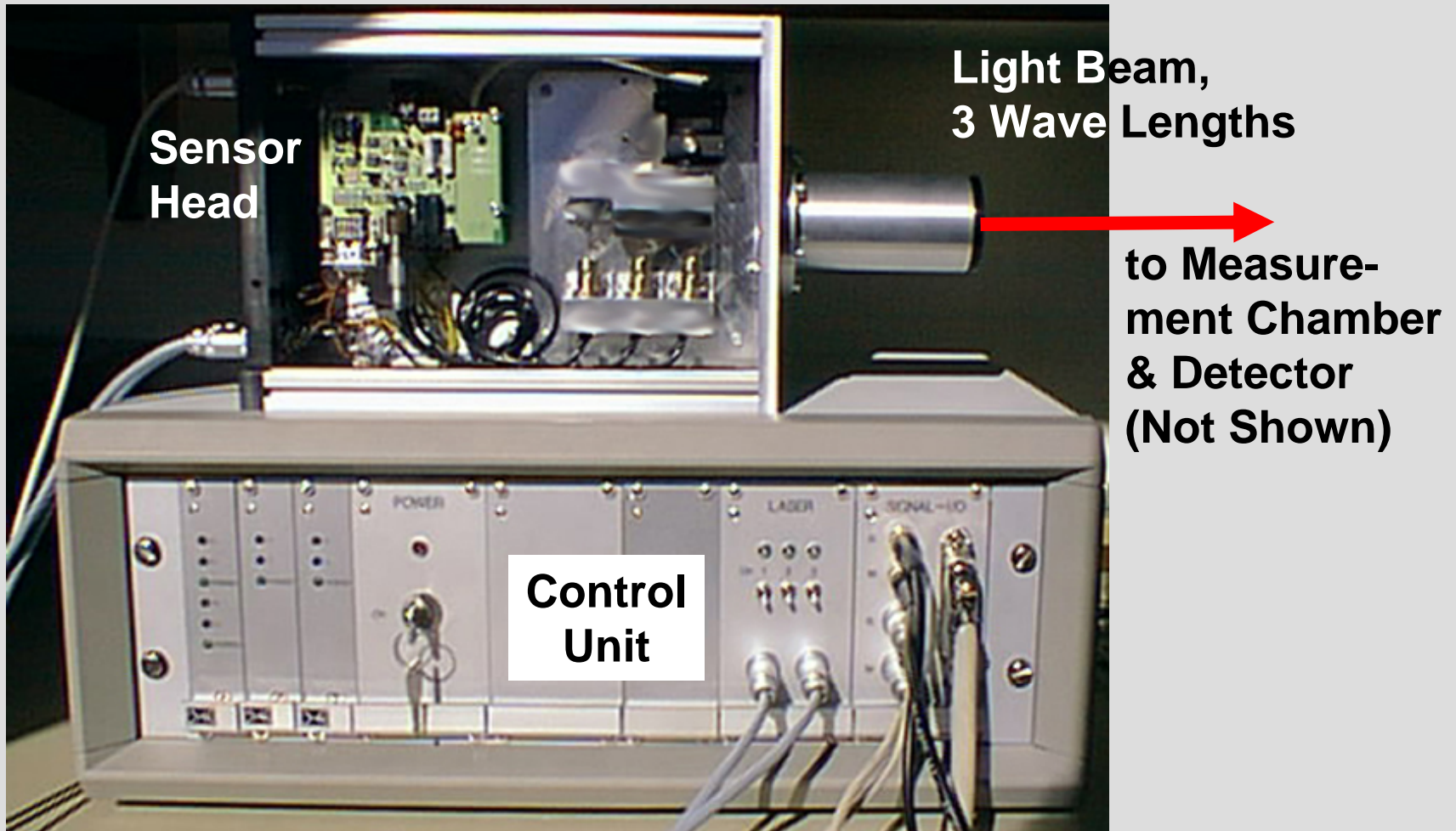
ECE Cycle

LD Engine

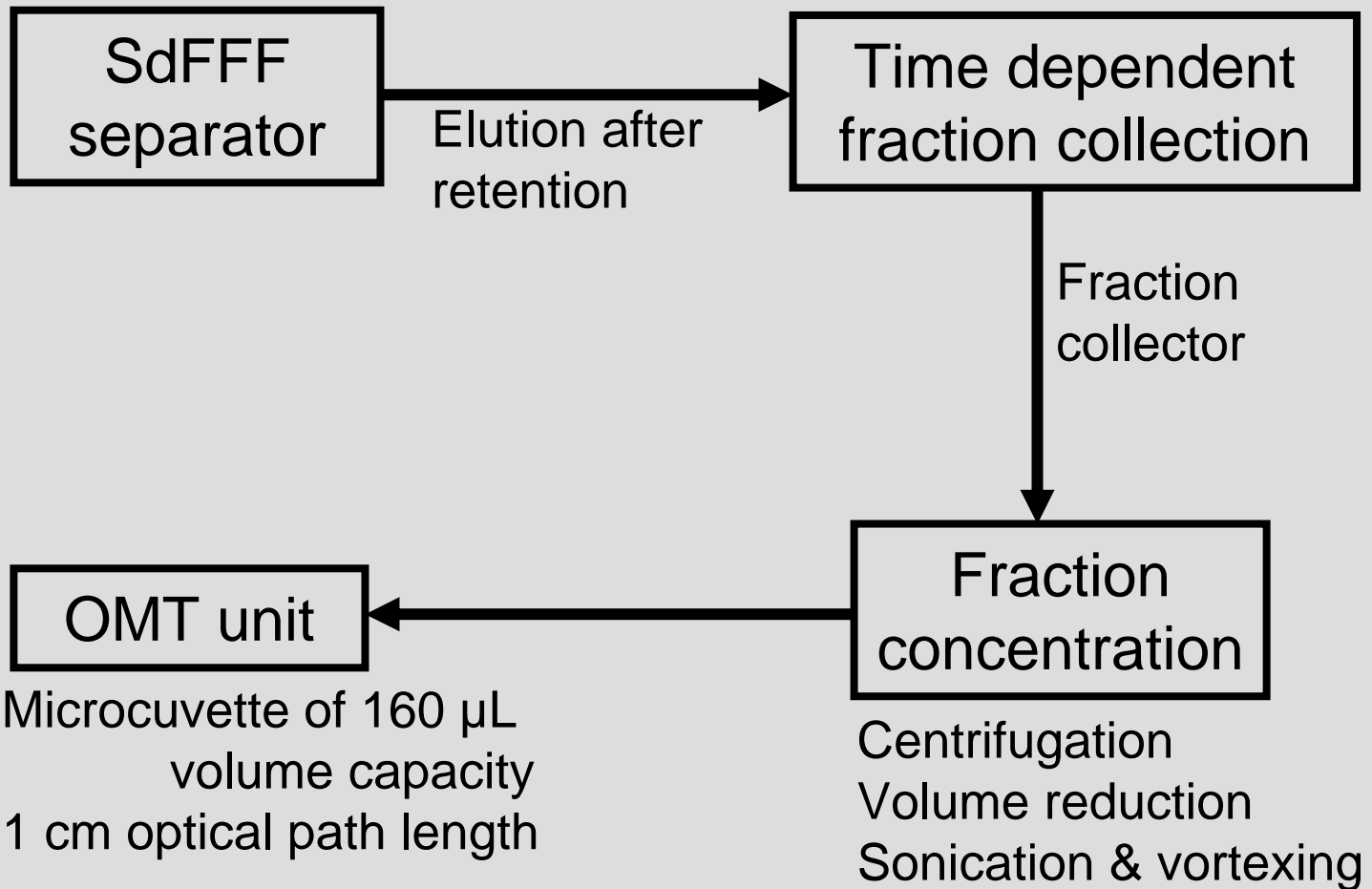
Schematic of the OMT



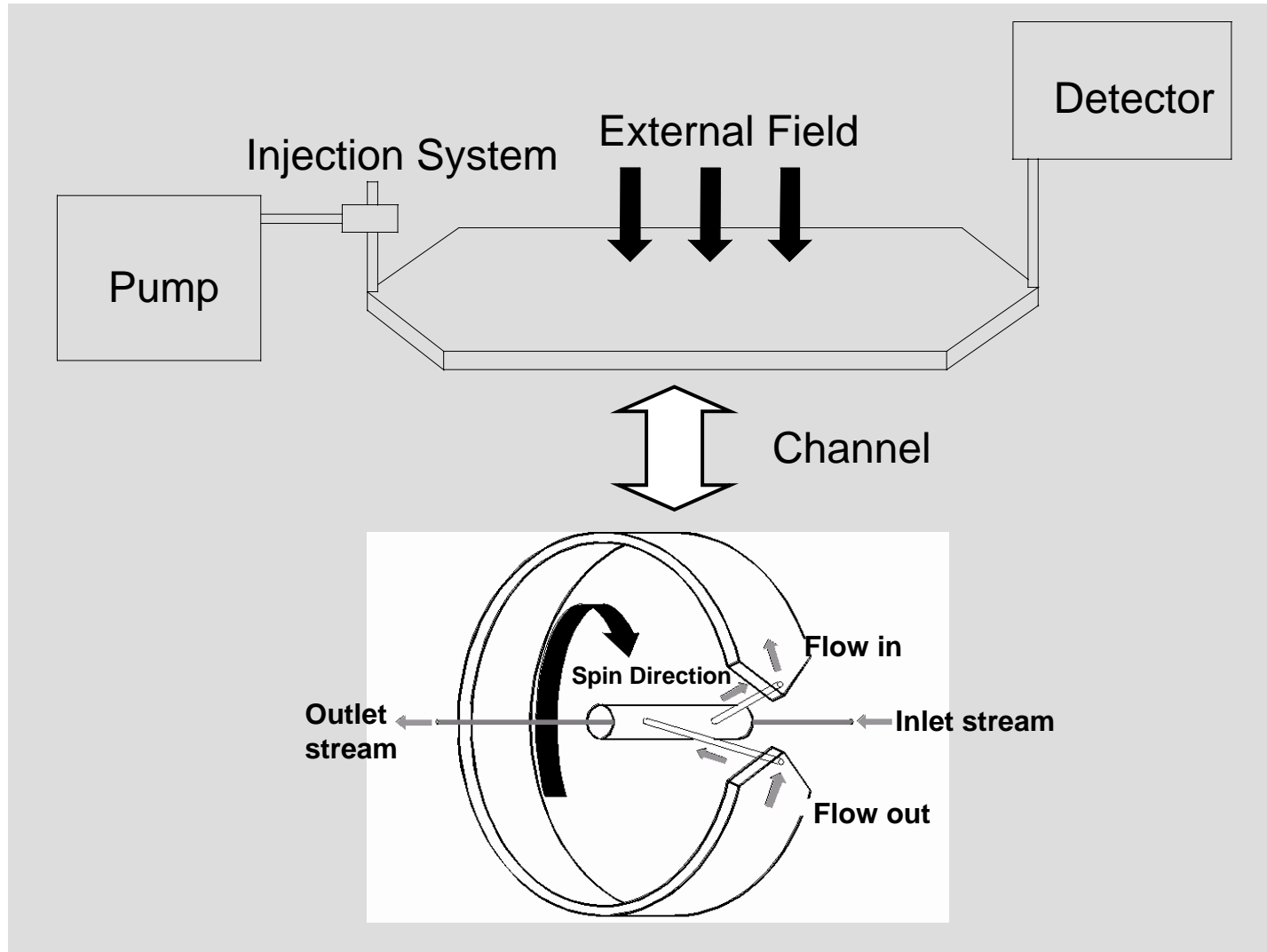
OMT: WIZARD DQL



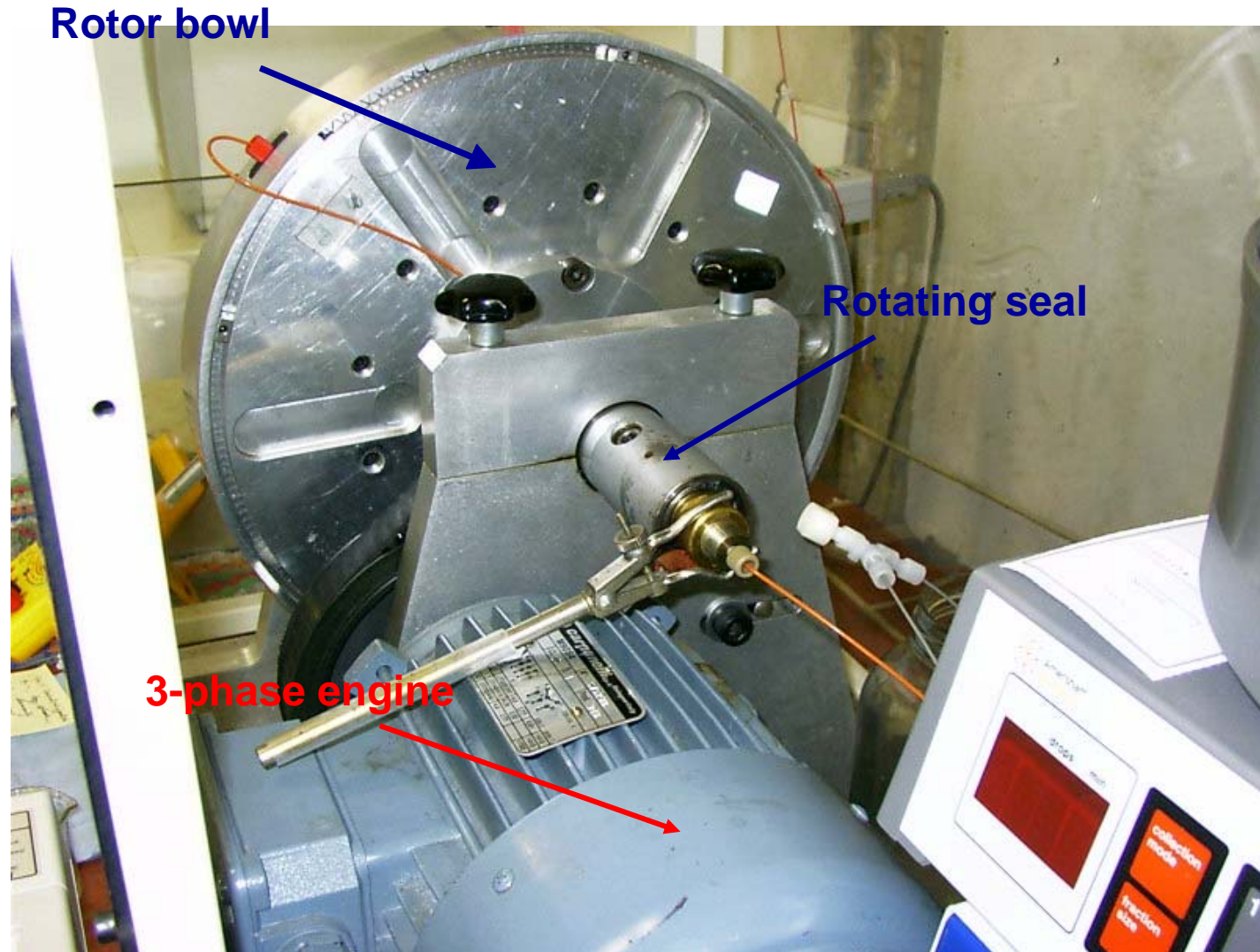
Off-line hyphenation set up



FFF System: SdFFF



SdFFF separator



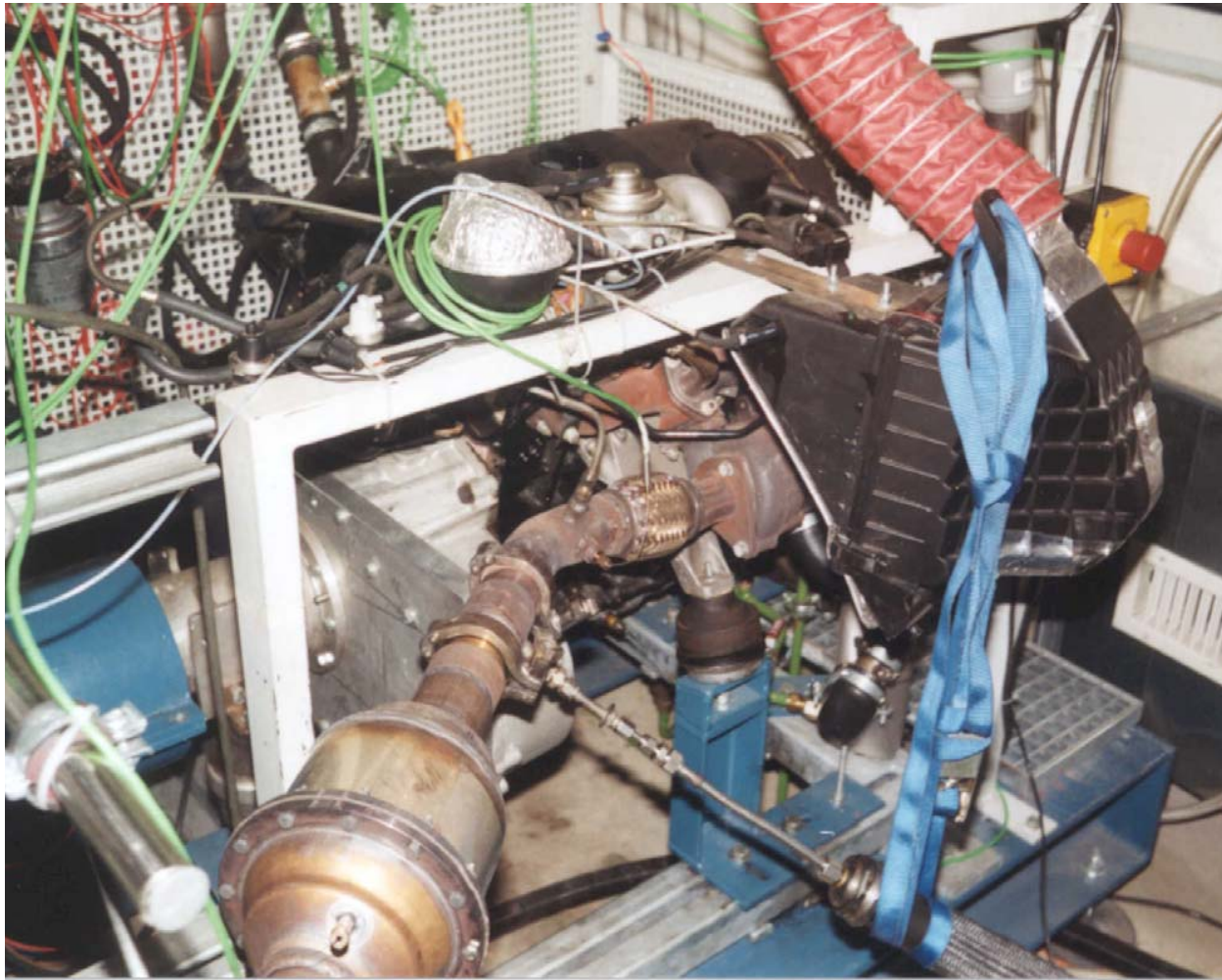
Back View

8th ETH Conf. on Combustion Generated Nanoparticles Aug. 2004

Diesel engine at CUTEC site

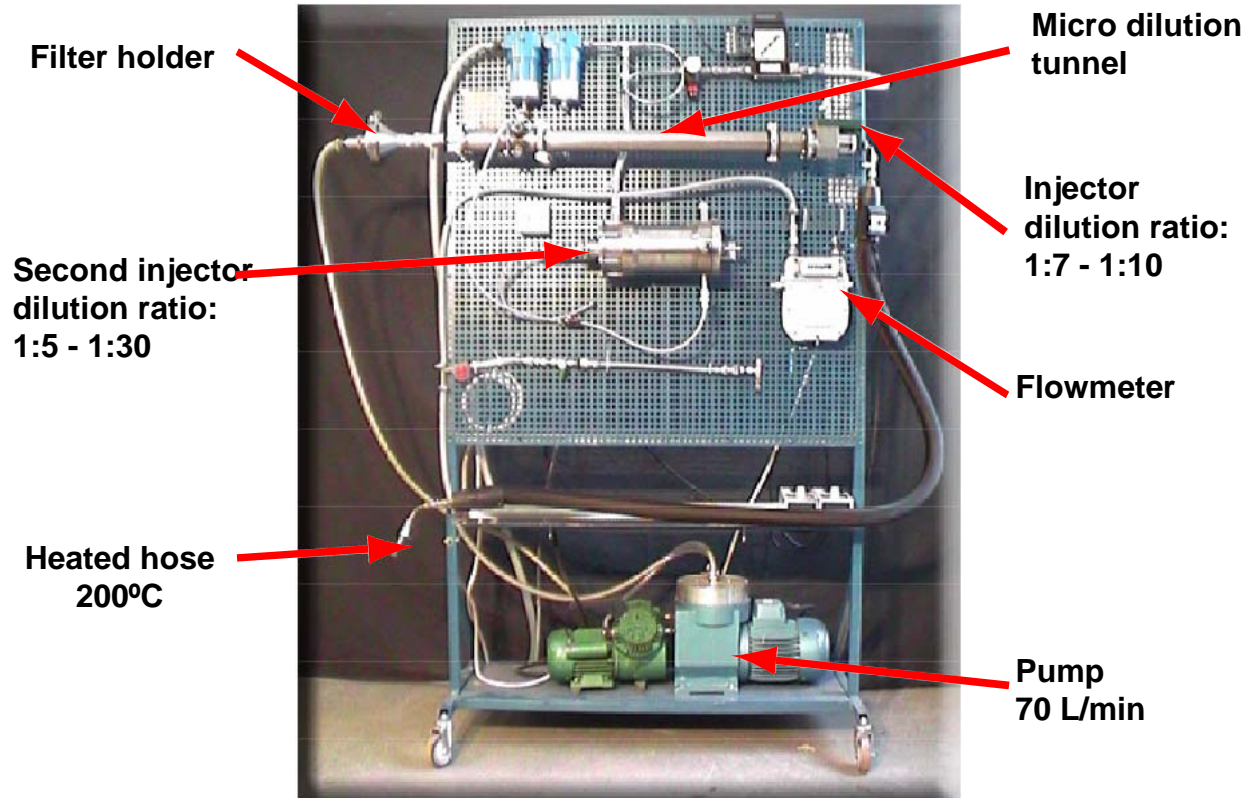
- **4 cylinder LD VW EURO III 85 KW engine, displacement volume 1.9 L**
- **Variable geometry torroidal technology (VGT)**
- **Exhaust gas recirculation (EGR)**
- **Pump unit injection (PUI)**

Engine Set-up at CUTEC Site



8th ETH Conf. on Combustion Generated Nanoparticles Aug. 2004

Dilution system

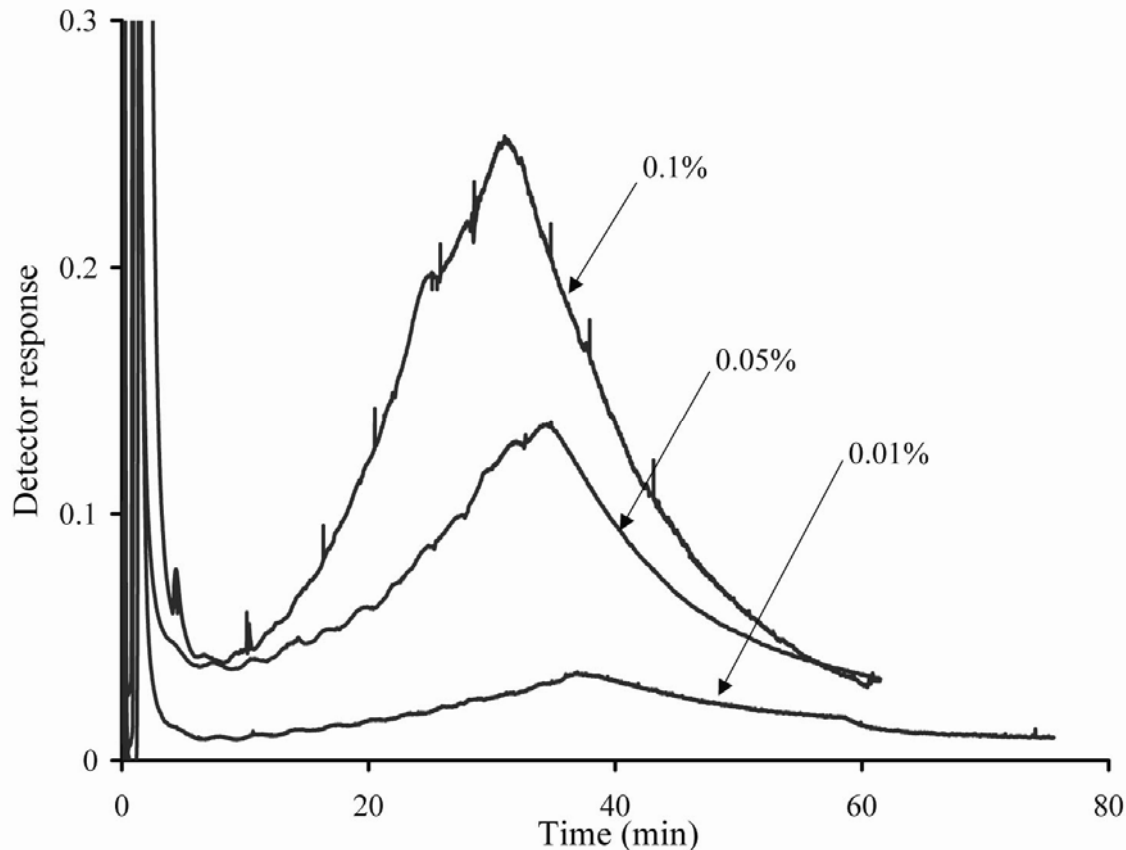


- Micro dilution tunnel
- Rapid mixing with the conditioned ambient air or dilution air
- Constant volume sampling (CVS)
- Teflon coated glass fiber filters Pallflex (70 mm diameter)

Sample preparation

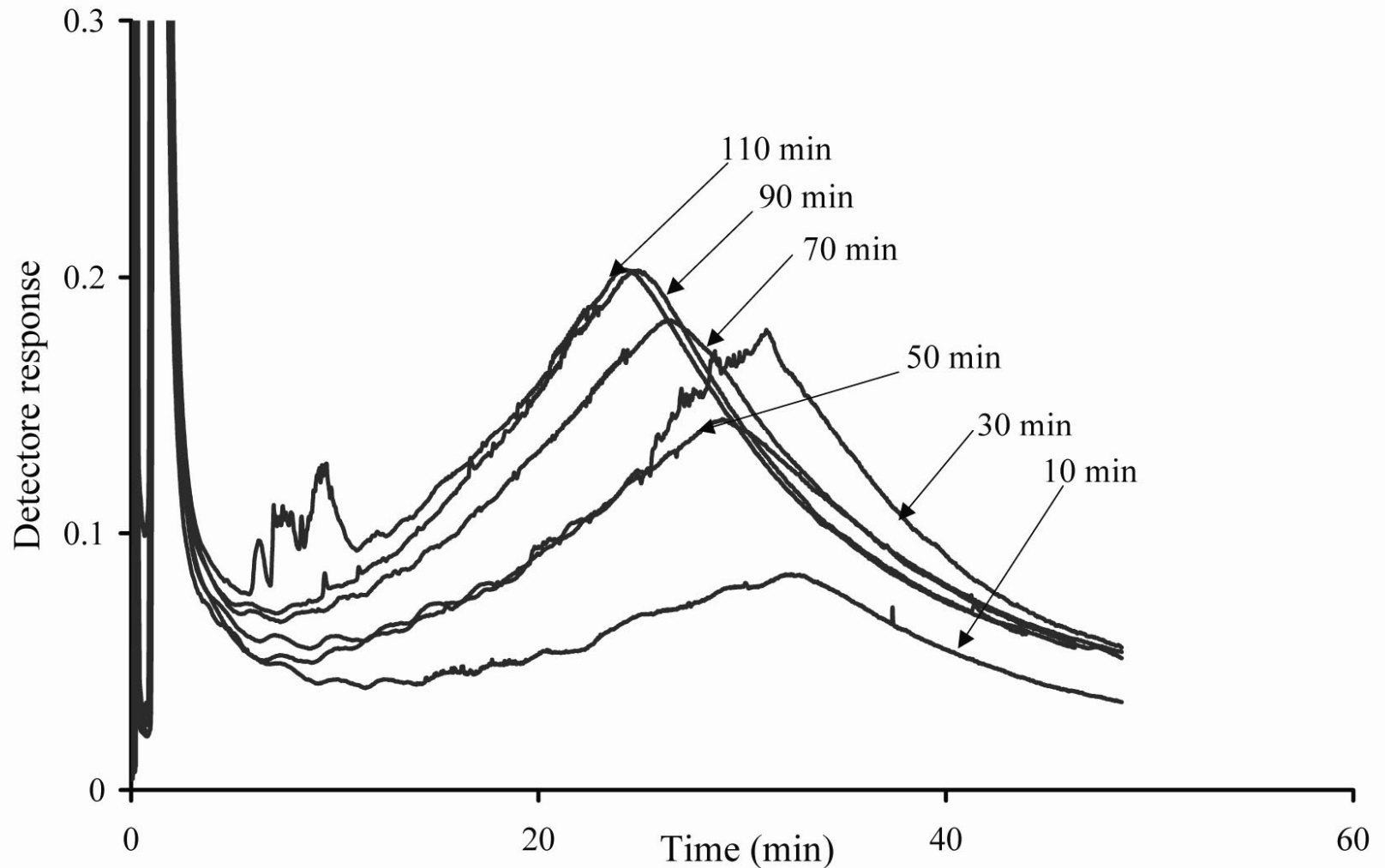
- Soot recovery by bath-sonication in 10 ml ethanol
- Mixture of ethanol+soot with 10 ml n-hexane
- After the removal of n-hexane, 5 ml distilled water containing 0.1% (w/v) and 0.02% NaN_3 are added
- Dispersion by 10 min bath-sonication
- Ethanol evaporation by heating at 70°C
- Sonication by a sonic dismembrator for 90 min and vortexing
- Carrier liquid and suspension media: doubly distilled water containing 0.1% (w/v) and 0.02% NaN_3
- Injection volume: 100 μL

Surfactant concentration effect

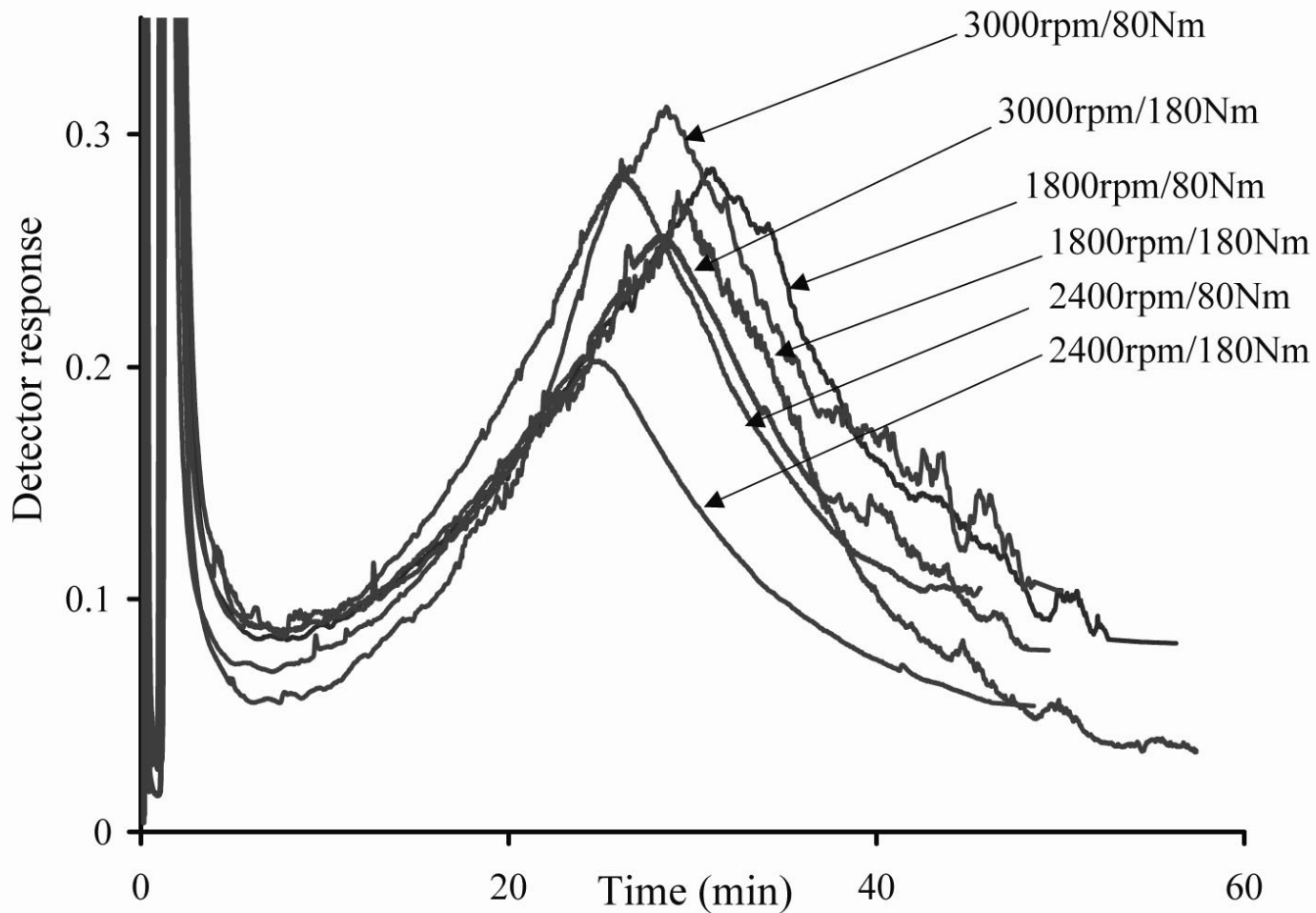


Elution conditions: initial field strength = 600g (1972 rpm);
injection flow rate=0.2 ml/min; Predecay time= 5 min; stop flow time=15 min;
final field strength=29.60g (439 rpm); elution flow rate= 1.2 ml/min

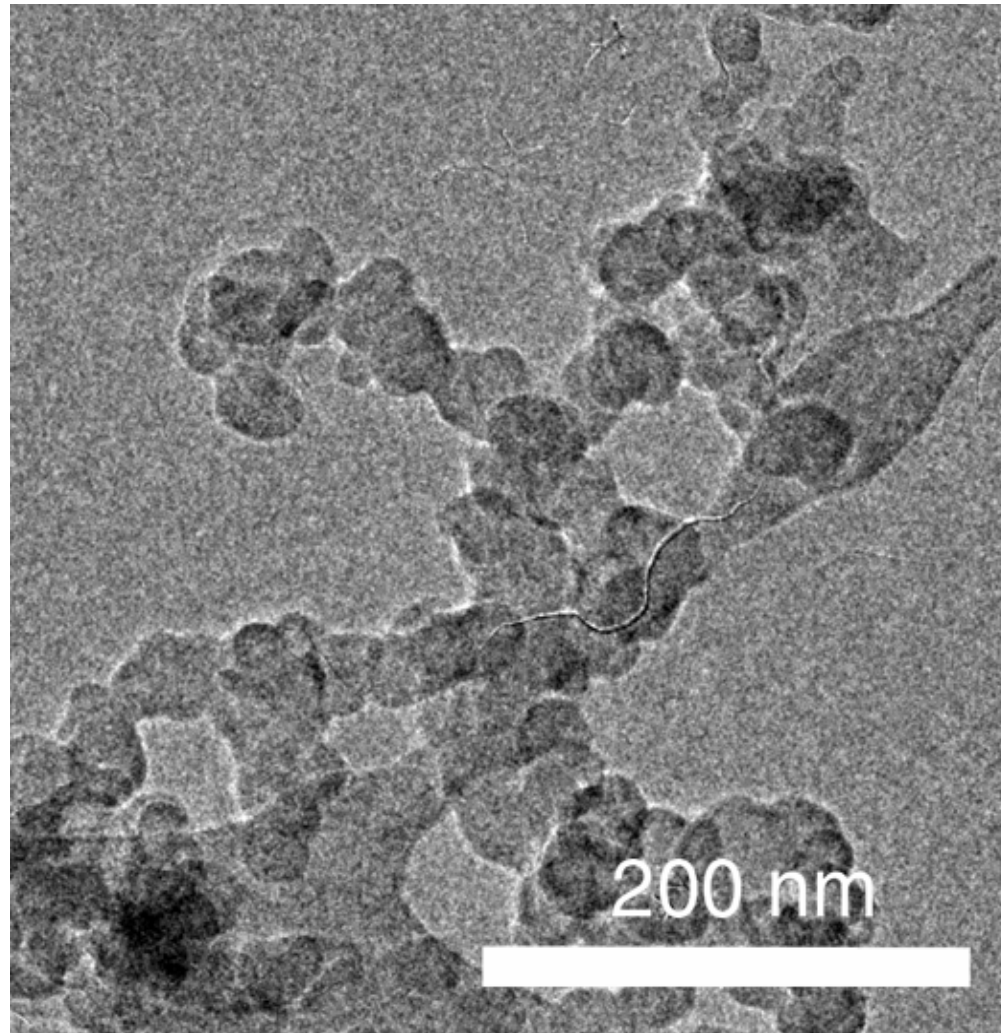
Sonication effect



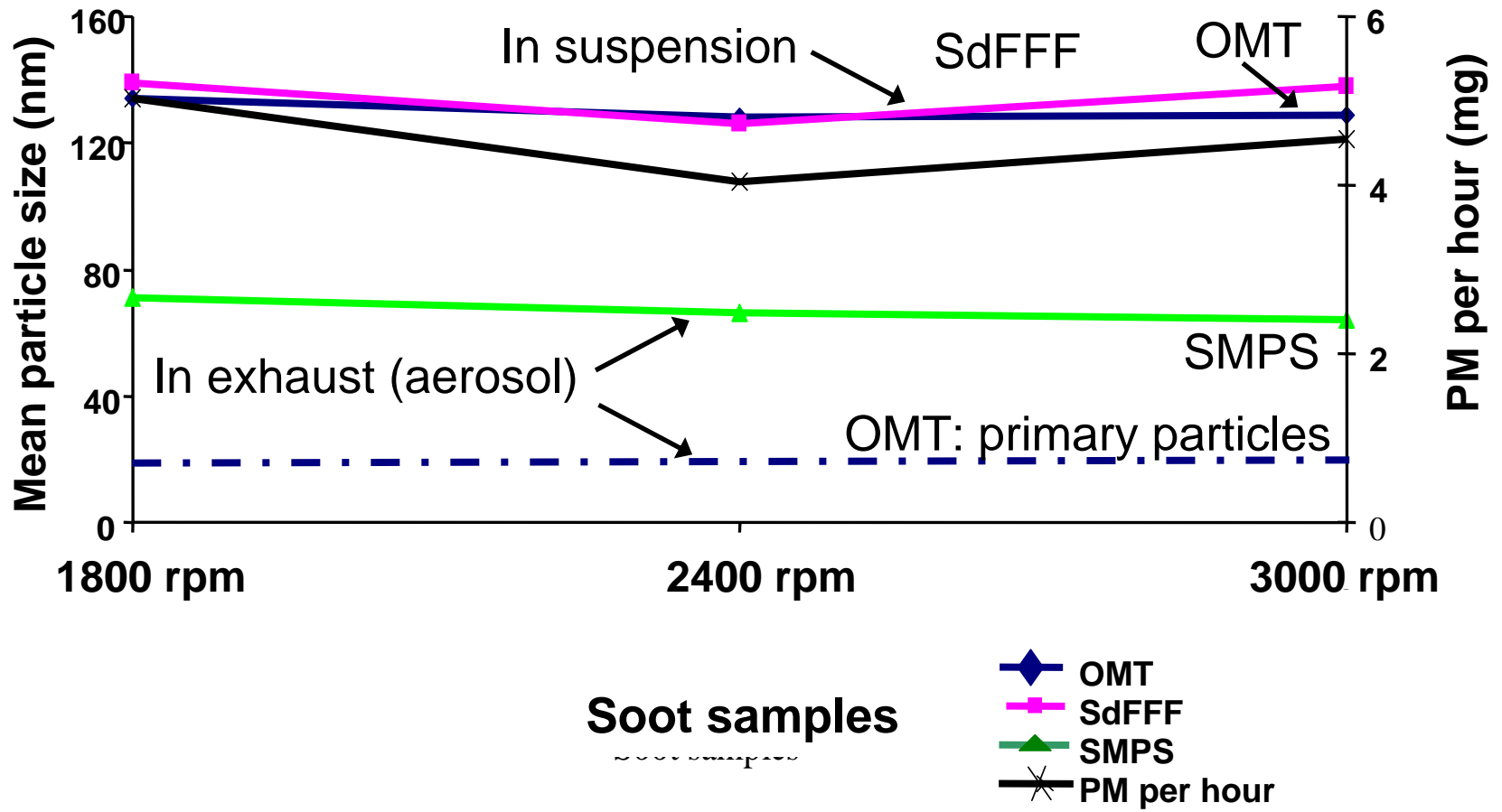
Soot elution by SdFFF



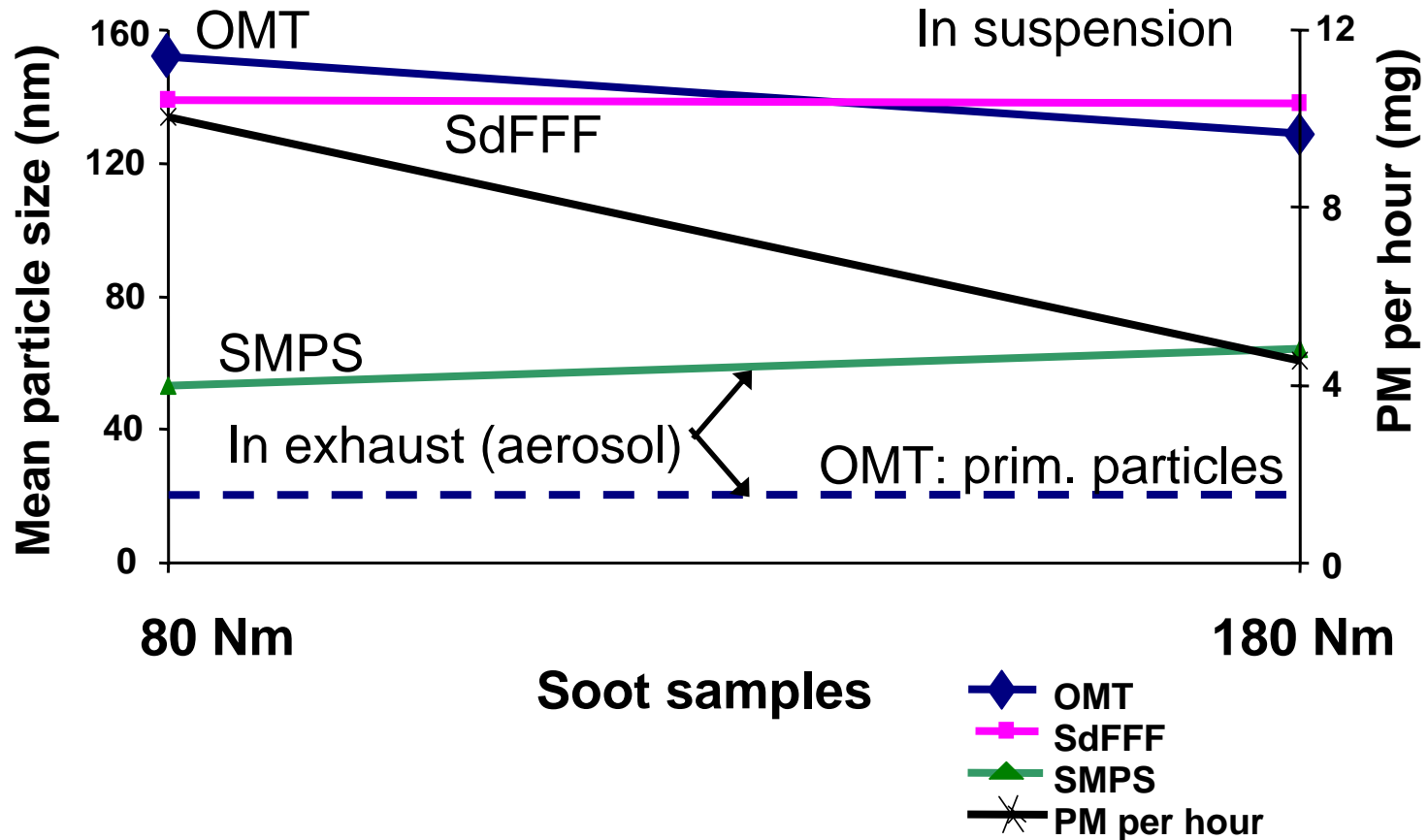
TEM pictures of soot (aerosol)



Engine speed effect on particle size at 180 Nm torque



Torque effect on particle size at 3000 rpm



Conclusion

- Soot particle size variation analyzed by OMT and SdFFF in the collected PM amount is related to the different engine load conditions
- The detected mean soot particle sizes in liquid suspensions differ appreciably to those in aerosols:
 - SdFFF and OMT measurements in liquid: 120 – 160 nm
 - OMT measurements in the raw exhaust: approx. 20 nm
(primary particles)
 - SMPS measurements in the diluted exhaust: 60 – 80 nm
- Different soot agglomerates in liquid and aerosol
- Surprisingly, the suspended soot particles keep specific characteristics related to engine load conditions