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

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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

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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
- Hot plate (metal)
- \( \frac{dT}{dx} \)
- Cold plate (metal)

Electrical FFF
- \( E \)

Flow FFF
- \( U \) (cross flow)

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Sedimentation FFF (SdFFF)

- Spin Direction
- Flow in
- Flow out
- Inlet stream
- Outlet stream
- Accumulation wall
- Thickness
- Parabolic flow profile
- Injection
- Exit port (to detector)
- Rotation
- Zone A
- Zone B
- Flow
- Parabolic flow profile

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Retention in the normal mode

External field

Flow

Parabolic flow profile

Accumulation wall

Zone A (slow) Zone B (fast)
Sedimentation field programming

Relaxation time

Accumulation wall

Detector signal (mV)

Time (min)

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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

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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
- \( Q_{\text{ext}} \) = extinction coefficient
- \( \lambda \) = wavelength
- \( n \) = refractive index
- \( p(r) \) = number distribution
Dispersion Quotient Technique (2)

OMT Principle

\[ DQ_1 = \frac{\ln \left( \frac{I}{I_0} \right)_{\lambda_1}}{\ln \left( \frac{I}{I_0} \right)_{\lambda_2}} = \frac{-N \cdot L \cdot \pi \cdot r^2 \cdot Q_{\text{ext}}(r, \lambda_1, n)}{-N \cdot L \cdot \pi \cdot r^2 \cdot \frac{Q_{\text{ext}}(r, \lambda_2, n)}{Q_{\text{ext}}(r, \lambda_2, n)}} \]

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Transient Measurements (ECE)

OMT Particle Analyzer (WIZARD-DQL)
ECE Cycle
LD Engine

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Schematic of the OMT

Central Unit
- POWER SUPPLY
- TIME CONTROL
- SIGNAL INTERFACE

Sensor Head
- LASER 1
- LASER 2
- LASER 3
- OPTICS

Data Acquisition

Measurement chamber
- Reference Detector

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OMT: WIZARD DQL

Light Beam, 3 Wave Lengths to Measurement Chamber & Detector (Not Shown)

Sensor Head

Control Unit

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Off-line hyphenation set up

SdFFF separator → Elution after retention → Time dependent fraction collection

Fraction collector → Fraction concentration

OMT unit
Microcuvette of 160 µL volume capacity
1 cm optical path length

Centrifugation
Volume reduction
Sonication & vortexing

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FFF System: SdFFF

Diagram showing the flow through the system:
- Injection System
- External Field
- Detector
- Channel
- Flow in
- Flow out
- Inlet stream
- Outlet stream
- Spin Direction

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SdFFF separator

Rotor bowl

Rotating seal

3-phase engine

Back View

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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

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Dilution system

- Filter holder
- Second injector dilution ratio: 1:5 - 1:30
- Heated hose 200ºC
- Pump 70 L/min
- Micro dilution tunnel
- Injector dilution ratio: 1:7 - 1:10
- Flowmeter

- 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)

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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% NaN₃ are added
- Dispersion by 10 min bath-sonication
- Ethanol evaporation by heating at 70ºC
- 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% NaN₃
- 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

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Sonication effect

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Soot elution by SdFFF

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TEM pictures of soot (aerosol)
Engine speed effect on particle size at 180 Nm torque

Soot samples

Mean particle size (nm)

PM per hour (mg)

In exhaust (aerosol)

In suspension

OMT: primary particles

SMPS

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Torque effect on particle size at 3000 rpm

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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

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