Chemical Properties and Formation Mechanisms of Volatile Nanoparticles from LDV

Shuichi Kubo, Masami Yamamoto, Satoru Chatani, Teruaki Kondoh, Satoshi Yamazaki
(TOYOTA CENTRAL R&D LABS., INC.)
Toshiaki Tanaka
(TOYOTA MOTOR CORP.)

1. INTRODUCTION

Nanoparticles formed in vehicle exhaust have received increasing attention due to their potential adverse health effects. It has been reported that there are carbonaceous nanoparticles and volatile nanoparticles (nucleation particles) observed in urban air and the vehicle exhaust, and nucleation particles consist mainly of organic and sulfur compounds. The nucleation particles exhausted from vehicles have been observed under idling, deceleration and high load conditions. But there are a lot of uncertain points for chemical properties and formation mechanisms of the nucleation particles.

We have conducted engine bench test, theoretical simulation and chemical analysis to clarify the formation mechanism of the nucleation particles under idling condition in a light-duty diesel engine system.

2. EXPERIMENTAL METHODS

Our engine system is a light-duty common-rail type DI diesel engine installing an oxidation catalyst and is controlled by a dynamometer. All experiments were performed at steady state. Engine-out and catalyst-out emissions were diluted by a NanoMet diluter and particle size distributions were measured by a SMPS.

In order to realize the chemical properties of the nucleation particles, we diluted the engine-out emissions under idling condition using a 2 stage-diluter and the diluted particles were classified by using a MOUDI and nano-MOUDI, and the size-classified particles were analyzed by using EPMA, FT-IR, GC-MS and TOF-SIMS.

We used three fundamental equations that treated nucleation, coagulation, condensation and vaporization to simulate the formation of nucleation particles at idle.

3. RESULTS and DISCUSSION

The number concentration of the nucleation particles at idle was dependent strongly on fuel property. The nucleation particles at idle were composed mainly of more than C18 hydrocarbons in fuel and existed at the exhaust gas temperature that exceeded 100 degree C in an exhaust-pipe before tailpipe-end and exhaust plume.

On the basis of the experimental result, we simulated the formation of the nucleation particles in the exhaust-pipe under idling condition. The result of simulation which treated the nucleation of $C_{26}H_{54}$ on behalf of fuel elements was in disagreement with the experimental result. The nucleation materials must have lower vapor pressure and lower surface tension than those of C26 n-paraffin to obtain an enough nucleation rate. Considering the existence of the nucleation material whose vapor pressure was 1/10,000 and surface tension was 70% to those of $C_{26}H_{54}$, we could simulate the formation of the nucleation particles in the exhaust-pipe under idling condition.

In order to study the existence of the nucleation materials which had the specific physical properties derived from the theoretical simulation, particles observed at idle were classified and the size-classified particles were analyzed.

Through FT-IR analysis, oxygenated hydrocarbons and phosphate were detected mainly in the range of 10-56nm in diameter, although hydrocarbons were observed in all the diameter ranges.

Based on the result of FT-IR analysis, we performed detailed analysis with TOF-SIMS. The percentage content of C-H-O hetero-compounds increased with the decrease in the range of the nanoparticle diameter. The hetero-compounds were estimated to be low temperature oxidation products which had the skeleton of high mass number fuel hydrocarbons and would be one of the nucleation materials under idling condition.

The percentage contents of Zn and phosphate increased in the nanoparticle diameter ranges. Zn and phosphate was estimated to be pyrolytic products of Zn-DTP oil additive. We evaluated a formation characteristic of the nucleation particles by the use of both engine oil containing the additives and that not containing the additives. The presence of the oil additives did not influence the formation of the nucleation particles under idling condition. The pyrolytic products of Zn-DTP oil additive would have low vapor pressure but were not the nucleation materials.

4. SUMMARY

We clarified the formation mechanism of the nucleation particles under idling condition in the light-duty diesel engine system.

The nucleation of the C-H-O hetero-compounds (oxygenated hydrocarbons) of fuel origin proceeds at the exhaust gas temperature that exceeds 100 degree C in the exhaust-pipe and the nucleation particles at idle are formed by the condensation of high boiling point hydrocarbons of fuel elements to nucleus. The nucleation particles at idle consist of a small amount of the oxygenated hydrocarbons of fuel origin and a large amount of more than C18 hydrocarbons of fuel elements.

8th ETH Conference
on Combustion Generated Nanoparticles

Condensation

Nucleation

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TOYOTA CENTRAL R&D LABS., INC.

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TOYOTA MOTOR CORPORATION

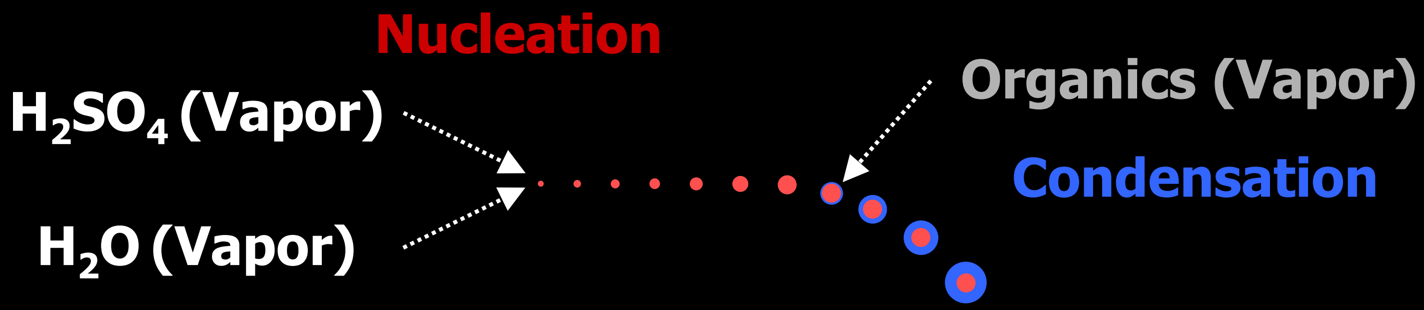
Introduction

- Nucleation particles were observed under following engine operation conditions.
  - Idling (non-load) condition
  - Deceleration condition
  - High load condition (with high S fuel and/or oxidation catalyst)

- But there are a lot of uncertain points for chemical properties and formation mechanisms of nucleation particles.

Nucleation Theory

- Formation mechanism of nucleation particles observed under high load conditions would be explained by H_2SO_4-H_2O binary homogeneous nucleation (BHN) theory.



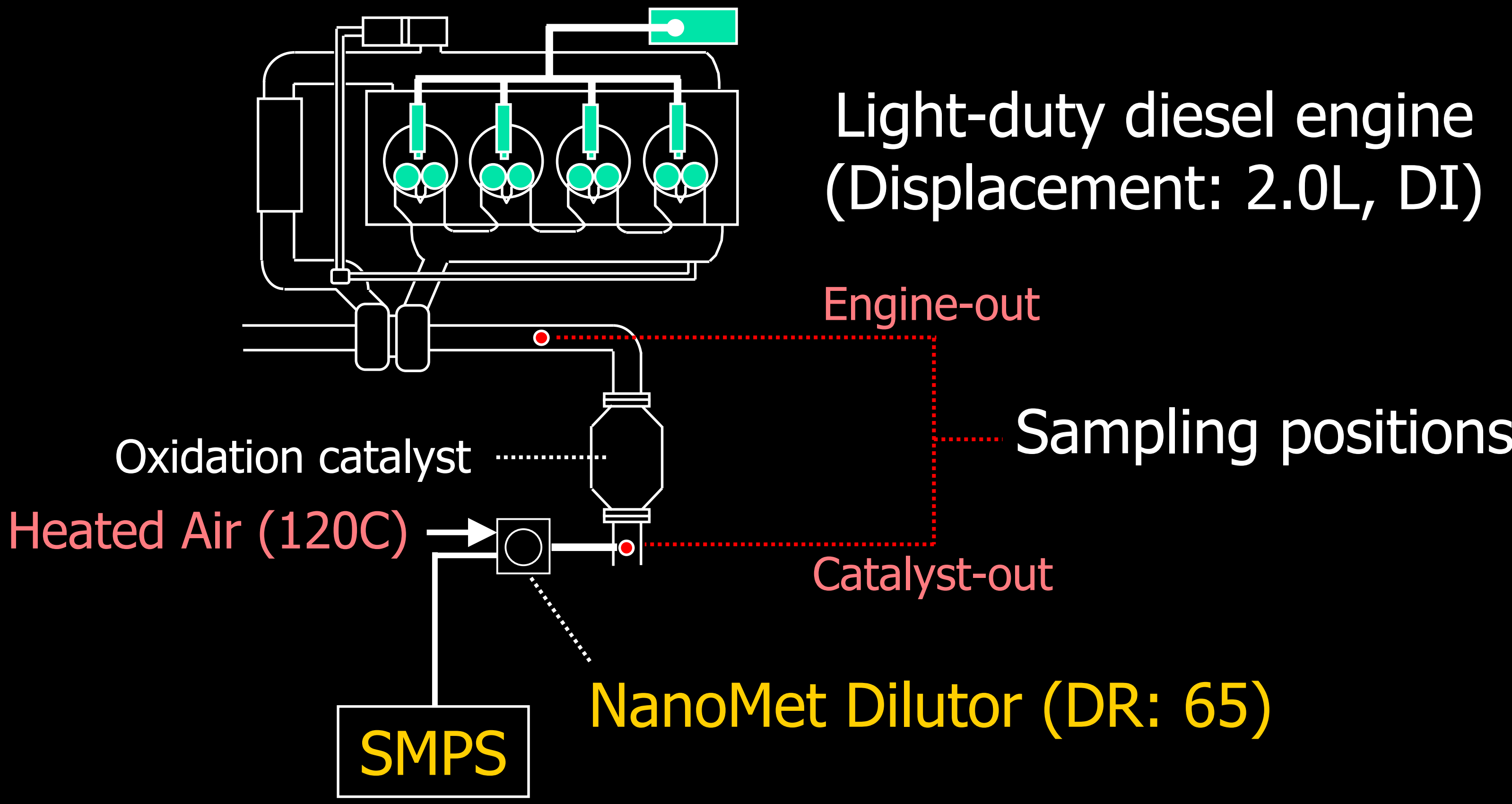
- In the case of idling and deceleration conditions, formation mechanisms of nucleation particles have not been explained theoretically yet.

Objective and Approach

- To clarify formation mechanism of nucleation particles under idling condition through following approaches.
  - Engine bench test
  - Simulation of nucleation particle formation
  - Chemical analysis of nucleation particles

1. Engine bench test

Diesel Engine Experiment

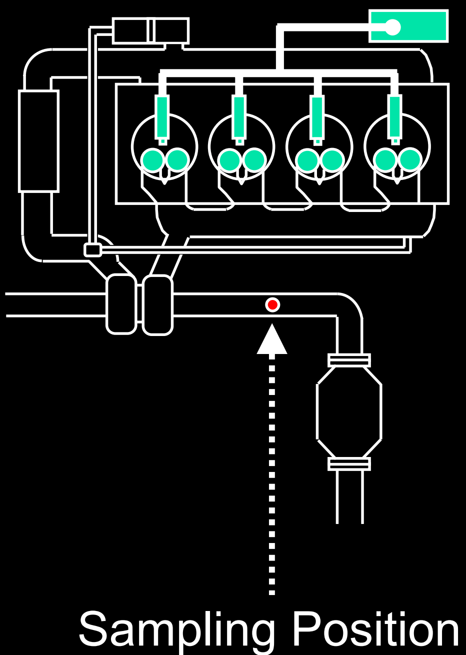


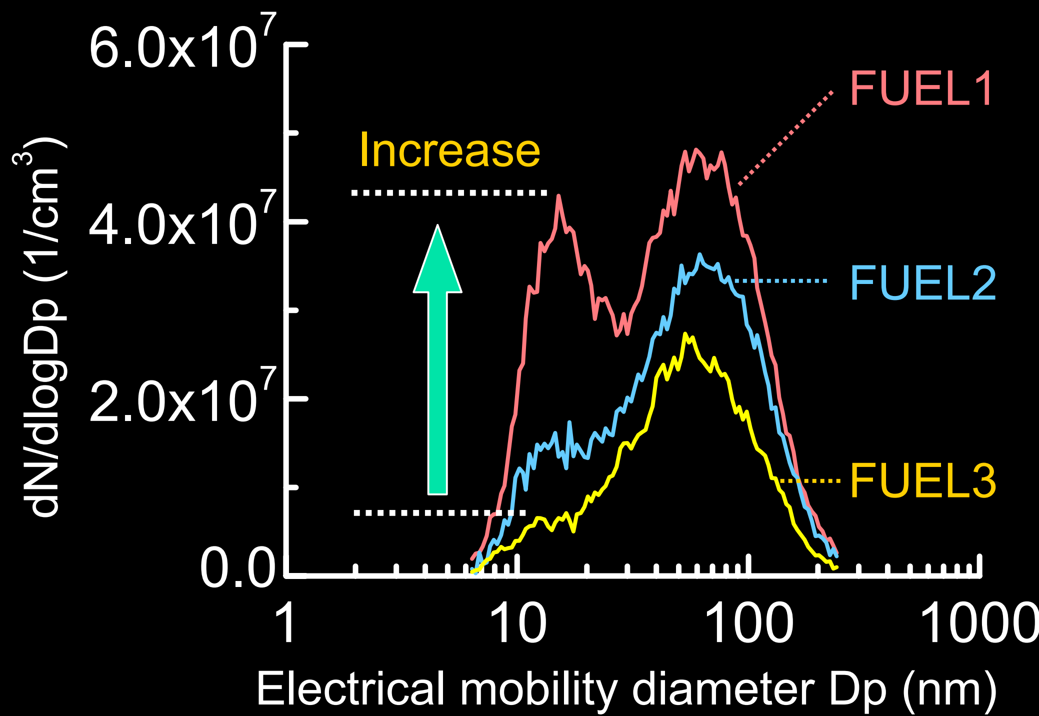
Diesel Fuel Specifications

	FUEL1 (High S)	FUEL2 (Conventional)	FUEL3 (Swedish Class 1)
Density @15deg C	0.8312	0.8323	0.810
Cetane Index	55	53	51.9
Aromatics vol%	27.6	18.5	2.4
Sulfur mass ppm	430	28	4
Distillation (deg C)			
10%	214.5	210.0	209.2
30	248.0	239.5	216.2
50	271.5	264.5	224.9
70	297.5	299.0	236.3
90	331.5	333.5	255.0
End point	370.5	358.5	280.4

Nucleation Particles at idle

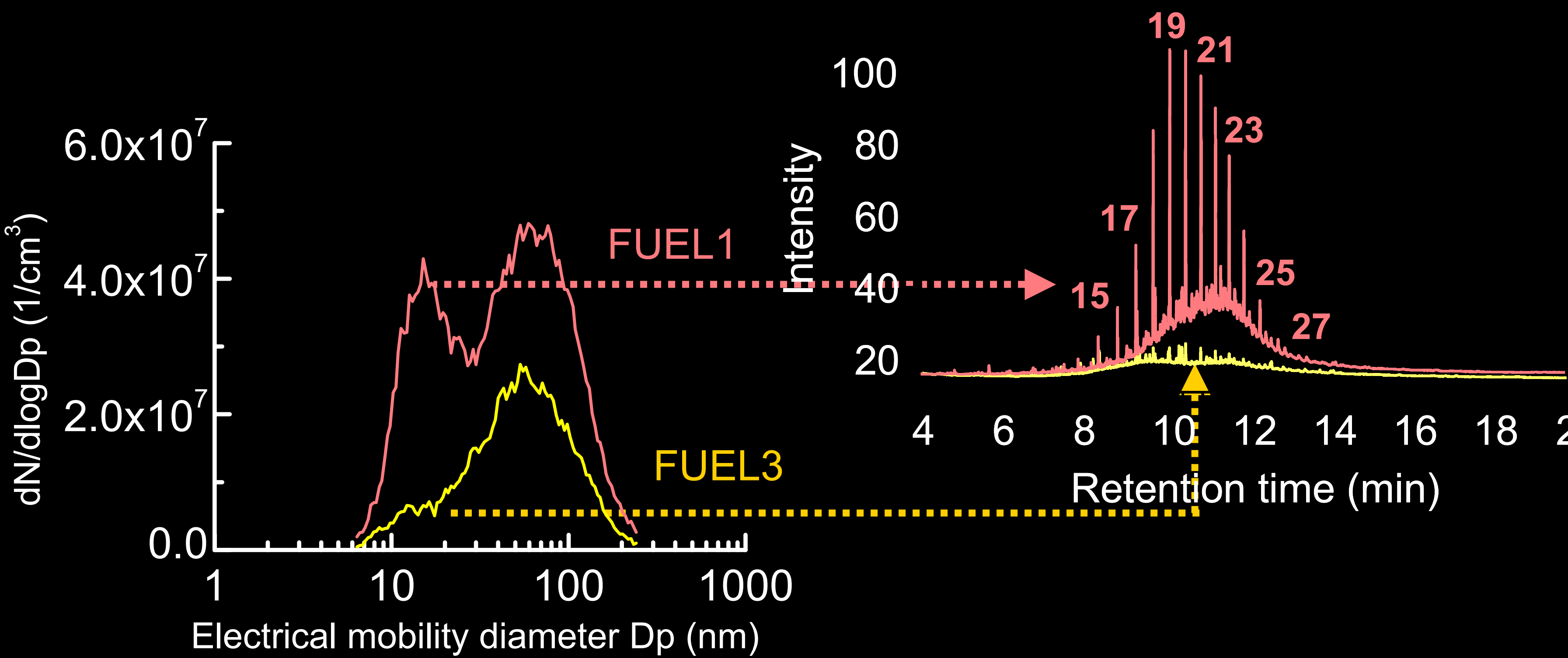
750rpm-0Nm





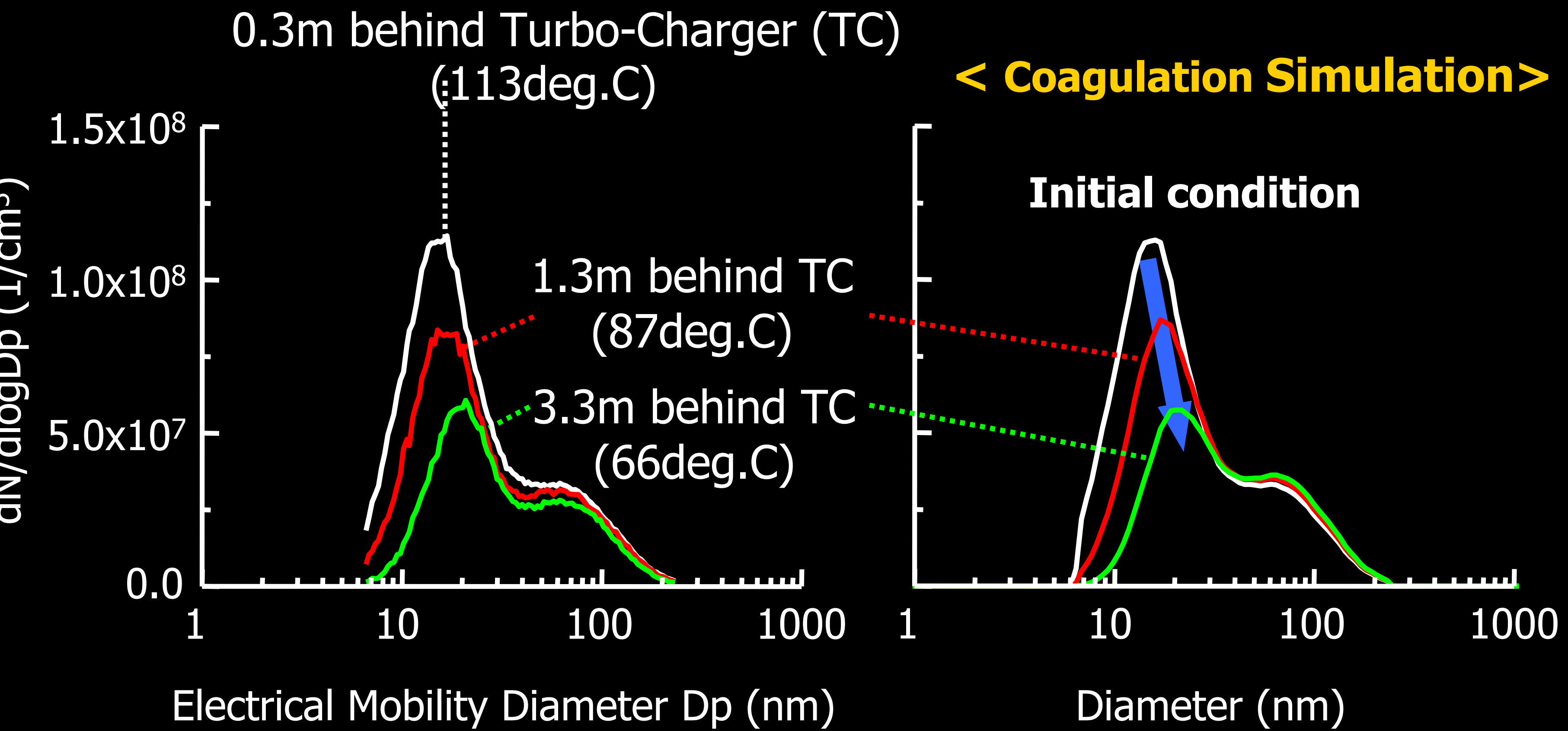
- Formation of nucleation particles at idle depends strongly on fuel property.

Chromatogram of SOF



- More than C18 hydrocarbons in fuel are main components of nucleation particles at idle.

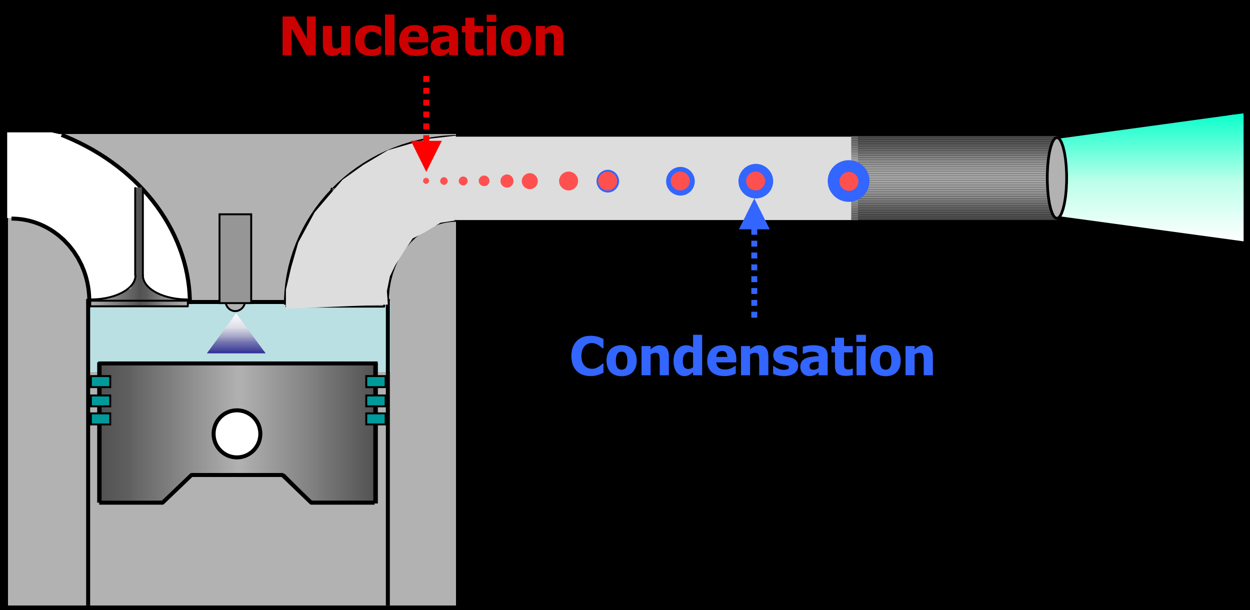
Where are Nucleation Particles formed?



- Nucleation particles exist at exhaust gas temperature that exceeds 100 C in exhaust-pipe.

Nucleation Particles at idle

- Nucleation particles exist at exhaust gas temperature that exceeds 100 C in exhaust-pipe.
- More than C18 hydrocarbons in fuel are main components of nucleation particles at idle.



2. Simulation of Nucleation Particles at Idle

$$\frac{\partial N_k}{\partial t} = \frac{1}{2}\sum_{j=1}^{k-1}\beta_{k-j,j}N_{k-j}N_j - N_k\sum_{j=1}^{n}\beta_{k,j}N_j$$

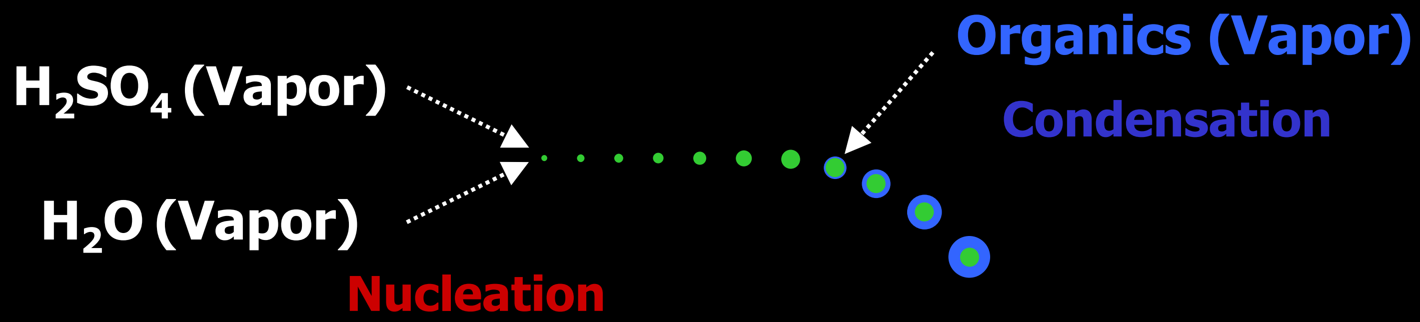
$$\frac{\partial m_k}{\partial t} = 2\pi D_i D_{pk} N_k f\left(Kn_k,\alpha\right)\left[C - C^{eq}\eta_k\right]$$

$$J = \left(\frac{2\sigma}{\pi m_1}\right)^{1/2}\frac{v_1 N_1^2}{S}\exp\left[-\frac{16\pi}{3}\frac{v_1^2\sigma^3}{\left(k_B T\right)^3\left(\ln S\right)^2}\right]$$

Nanoparticle formation Mechanisms

- Formation mechanism of nucleation particles at idle cannot be explained by BHN theory as nucleation particles form at exhaust gas temperature that exceeds 100 C in exhaust-pipe.

- Binary Homogeneous Nucleation (BHN) theory -



Hydrocarbon Nucleation

- We tried to simulate formation of nucleation particles at idle through hydrocarbon nucleation by following three fundamental equations.

Coagulation

$$\frac{\partial N_k}{\partial t} = \frac{1}{2}\sum_{j=1}^{k-1}\beta_{k-j,j}N_{k-j}N_j - N_k\sum_{j=1}^{n}\beta_{k,j}N_j$$

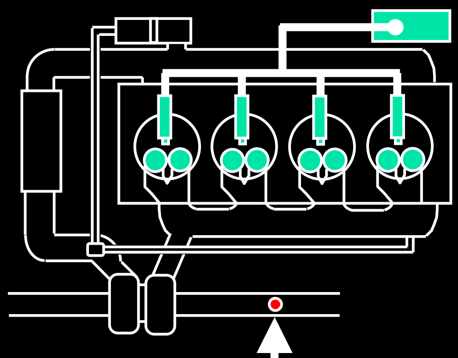
Condensation /Vaporization

$$\frac{\partial m_k}{\partial t} = 2\pi D_i D_{pk} N_k f\left(Kn_k,\alpha\right)\left[C - C^{eq}\eta_k\right]$$

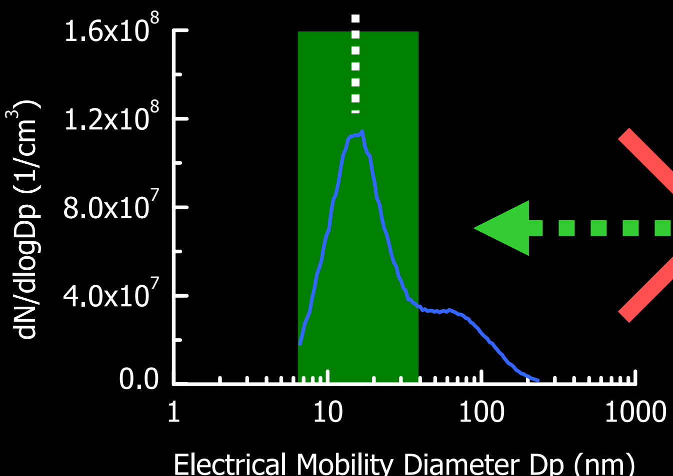
Nucleation

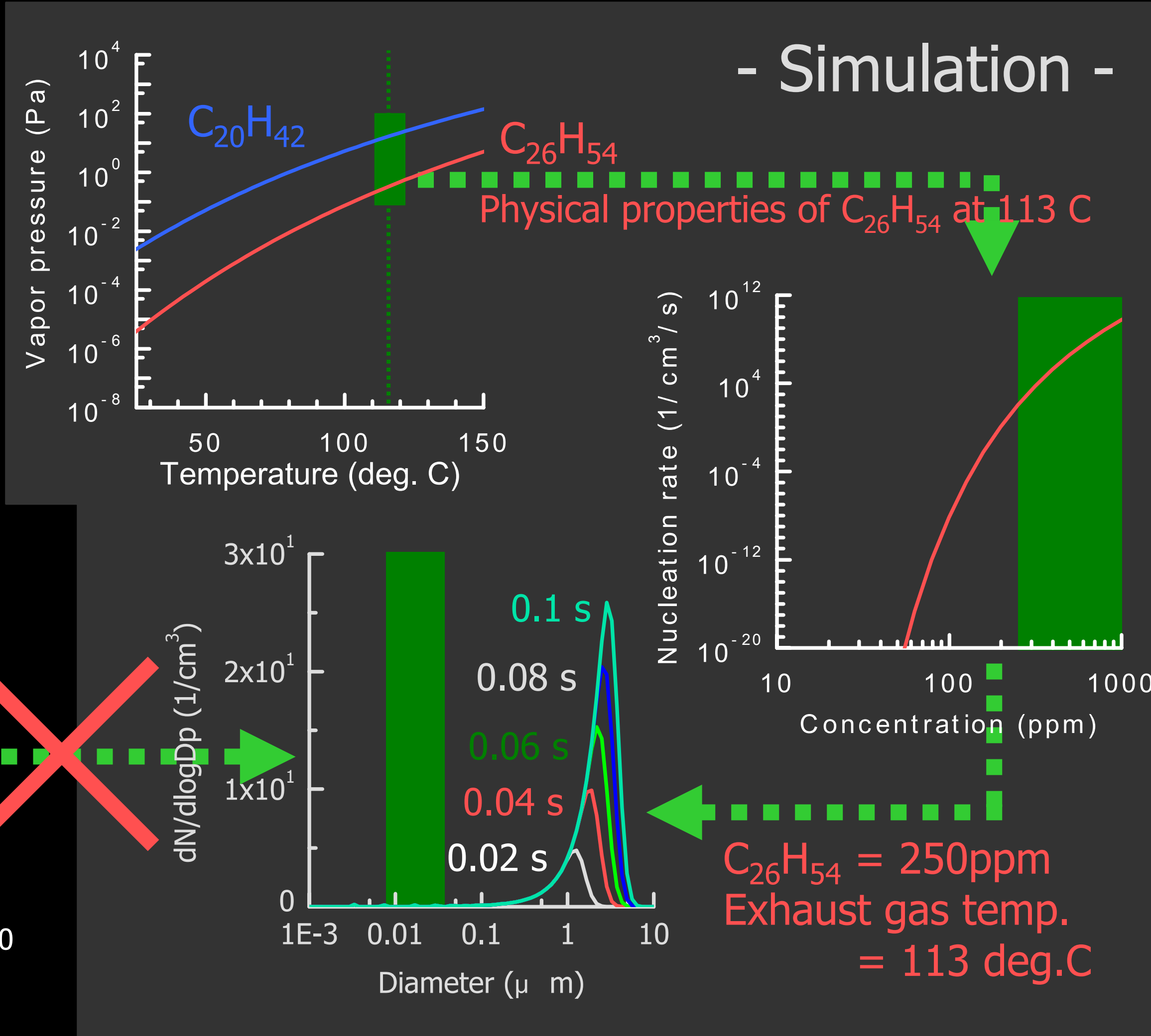
$$J = \left(\frac{2\sigma}{\pi m_1}\right)^{1/2}\frac{v_1 N_1^2}{S}\exp\left[-\frac{16\pi}{3}\frac{v_1^2\sigma^3}{\left(k_B T\right)^3\left(\ln S\right)^2}\right]$$

Nanoparticle Formation at Idle



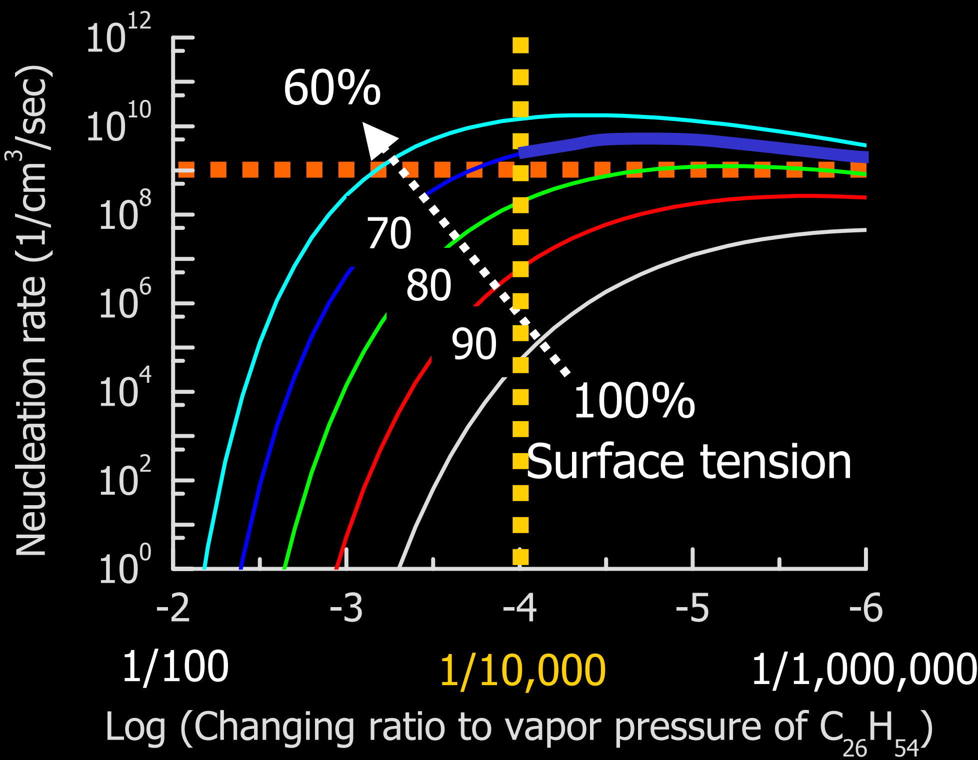
Exhaust gas Temp.=113C





This result suggests the existence of other nucleation materials

Nucleation Rate



/ Temperature: 113 deg. C ,that is exhaust gas temp at idle.
/ Concentration: 0.25 ppm

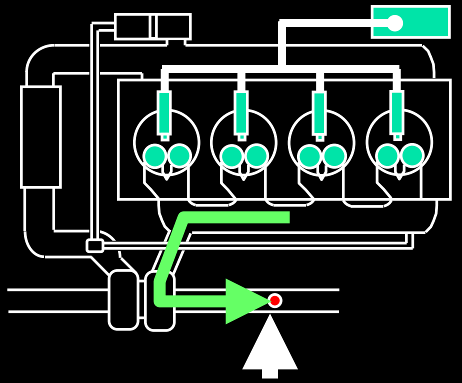
Effect of vapor pressure and surface tension on nucleation rate.

Nucleation rate needs 10^9 to get more than 10^8 part/cm^3 nanoparticles at idle.

- Considering 1/10,000 in vapor pressure and 70% in surface tension to those of $C_{26}H_{54}$, we can simulate enough nucleation rate.

Simulation of Nanoparticle Formation at Idle

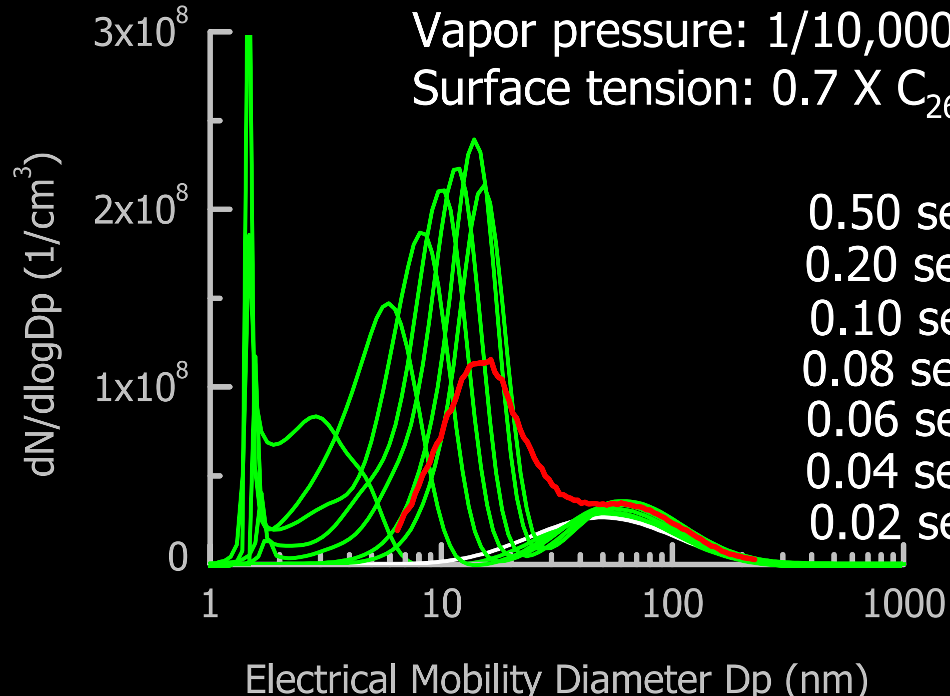
750rpm-0Nm (idle)



Exhaust gas Temp.=113C

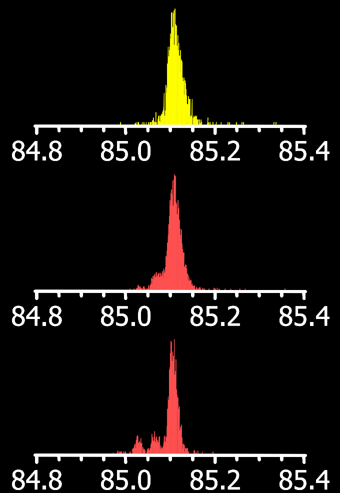
< Initial value >

- Soot maximum conc.: 2E+7 part./cm^3 with log-normal shape
- Nucleation material (NM) : 0.25ppm
  Vapor pressure: 1/10,000 X $C_{26}H_{54}$
  Surface tension: 0.7 X $C_{26}H_{54}$



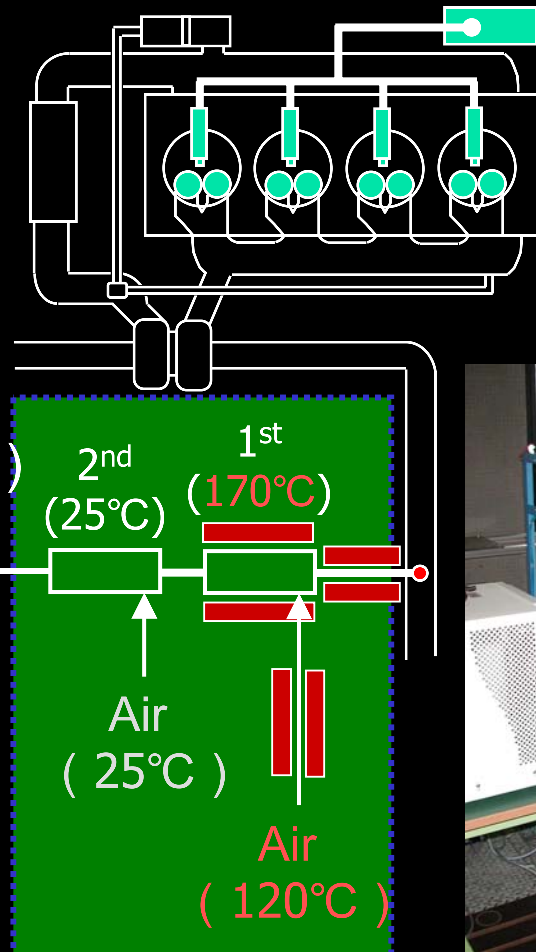
- Considering specific physical properties of NM, simulation result is in good agreement with experimental result.

3. Chemical Analysis of Nucleation Particles at idle



Experimental Set-up

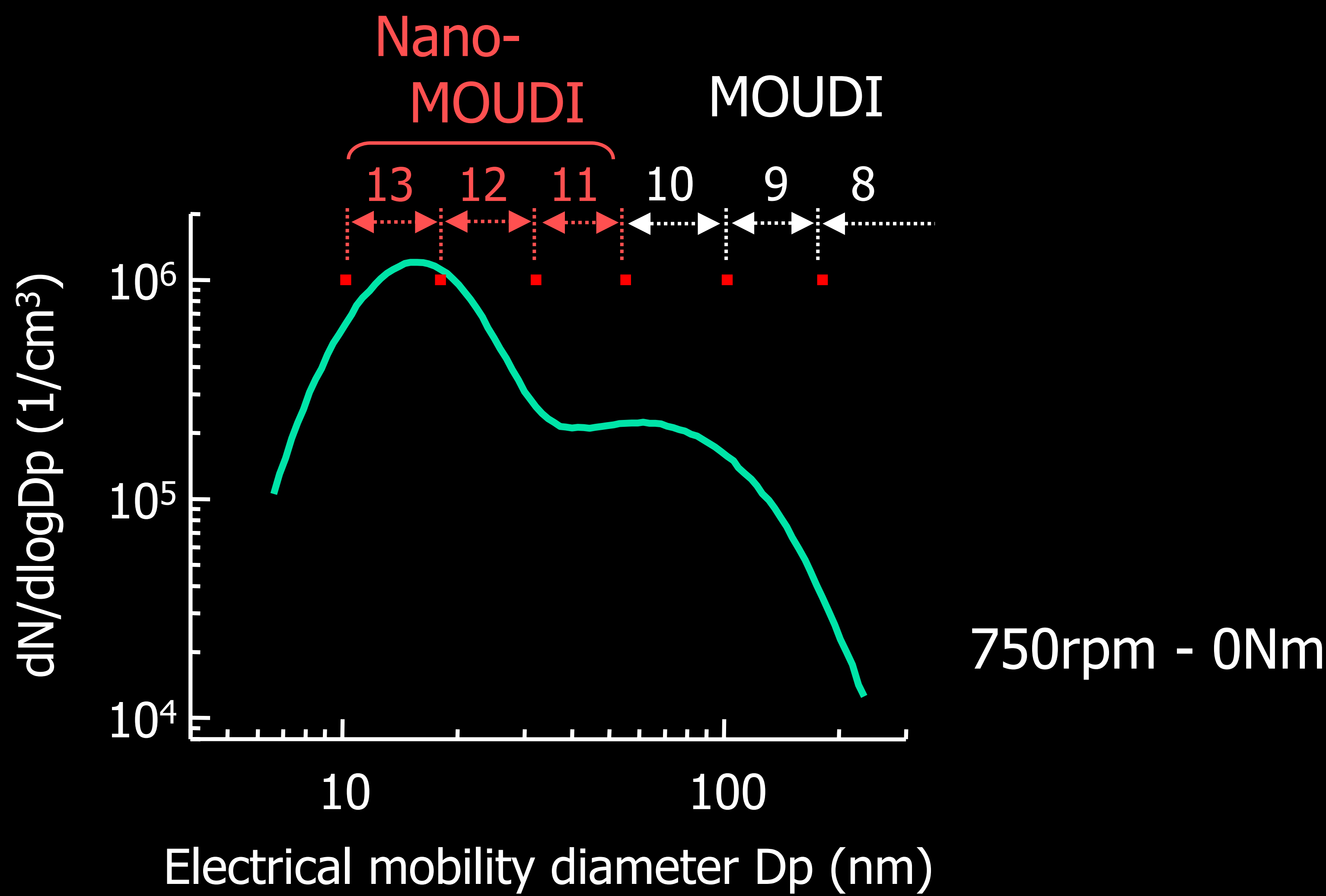
- Engine operating condition : 750rpm-0Nm
- Fuel : S=420ppm diesel fuel



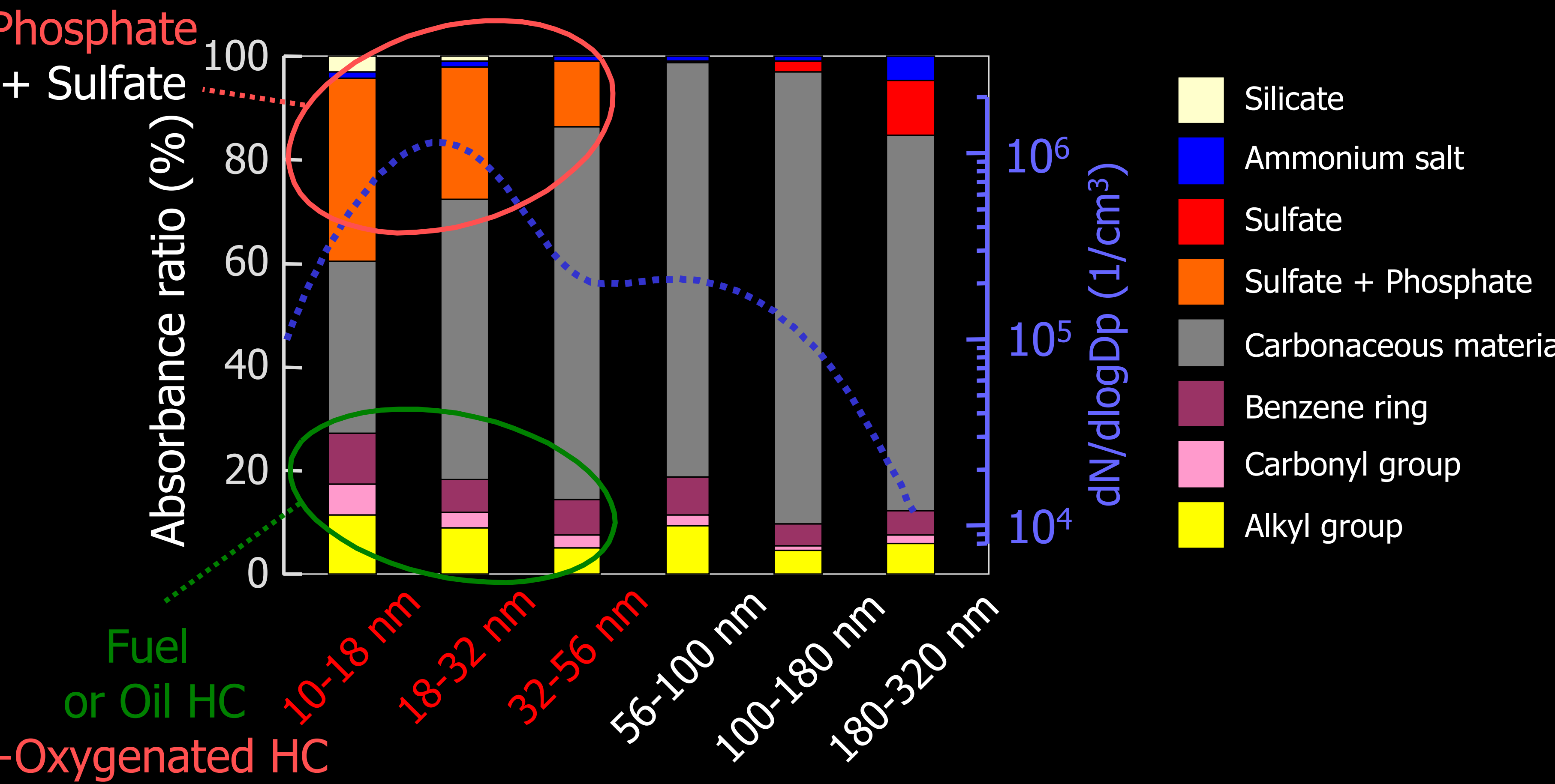
Sampling period : 5 hours

* SMPS: Scanning Mobility Particle Sizer

Classified Particle Diameter Ranges

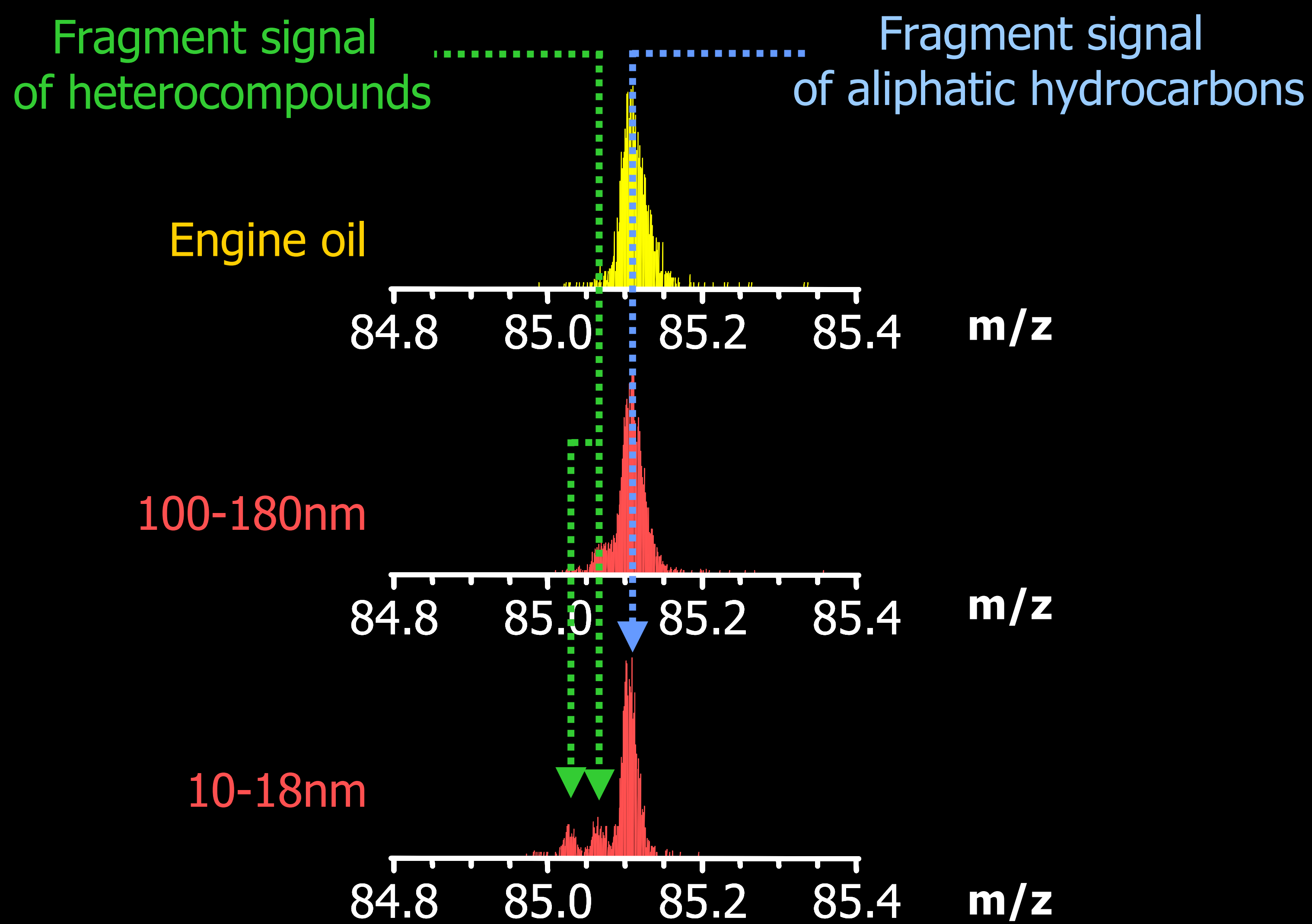


FT-IR Analysis of Classified Particles

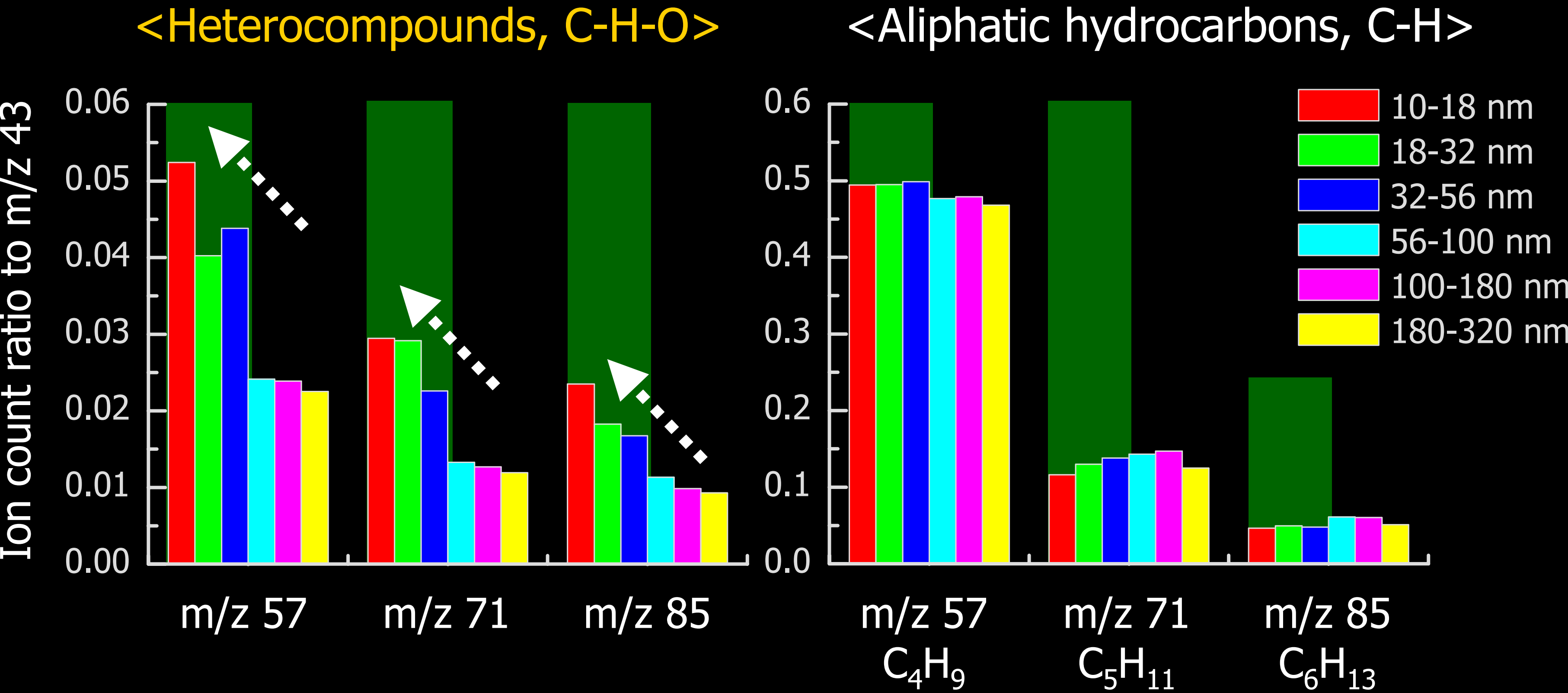


- Phosphate and oxygenated HCs are detected mainly in the range of 10-56nm in diameter.

TOF-SIMS Analysis for Heterocompounds

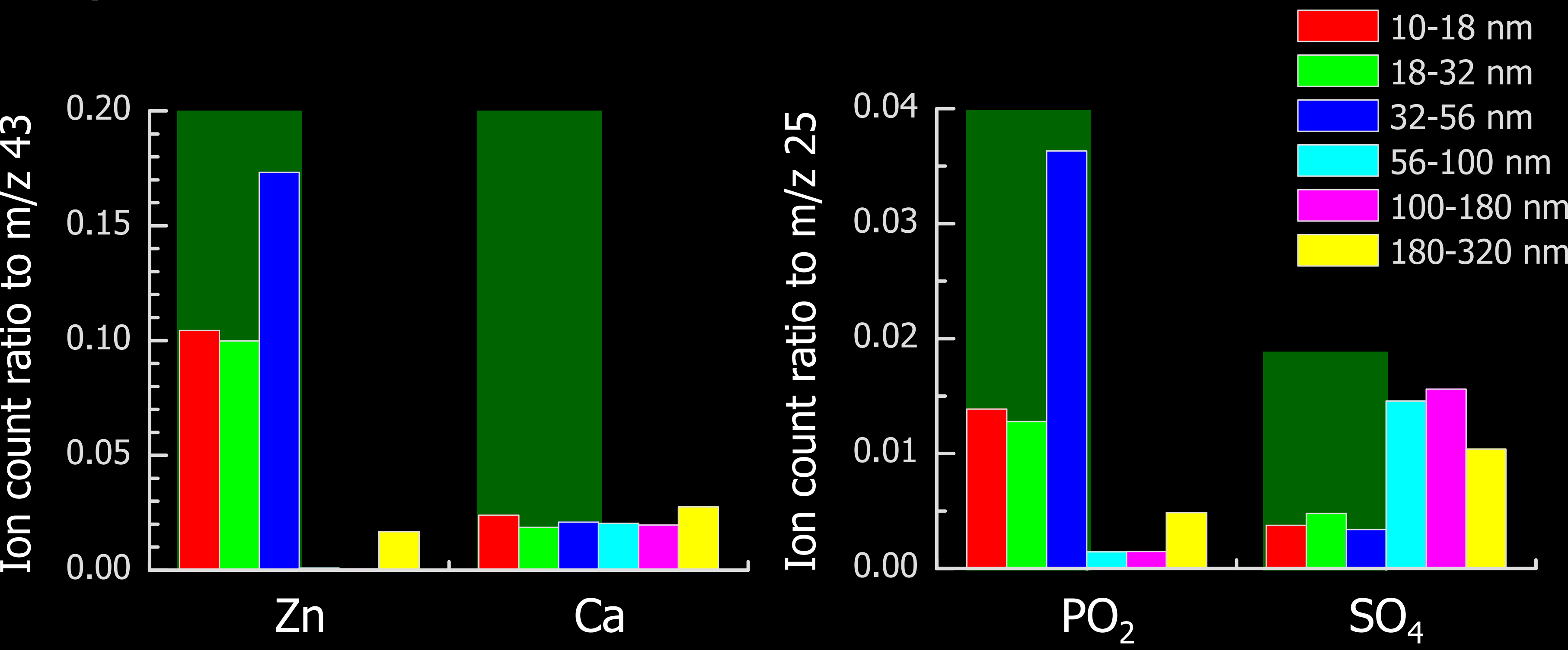


Heterocompounds in Nucleation particles



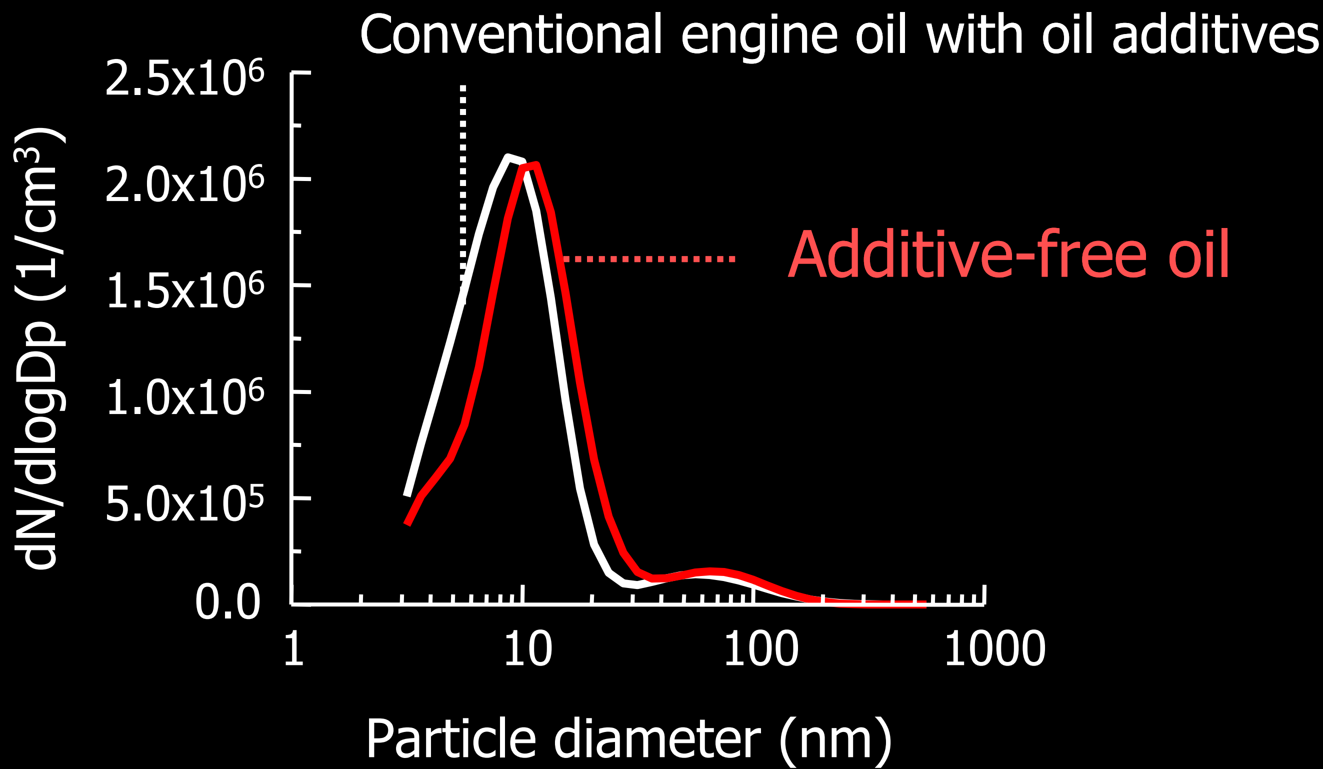
- Percentage content of hetero-compound increases in the range of nanoparticle diameter.

Effect of Inorganic Compounds



- Percentage contents of Zn and PO_2 increase in the range of nanoparticle diameter.
- Zn and PO_2 would be pyrolytic products of oil additive (Zn-DTP).

Nucleation at Idle and Oil Additives



- Oil additives do not contribute to nucleation of nanoparticles at idle.

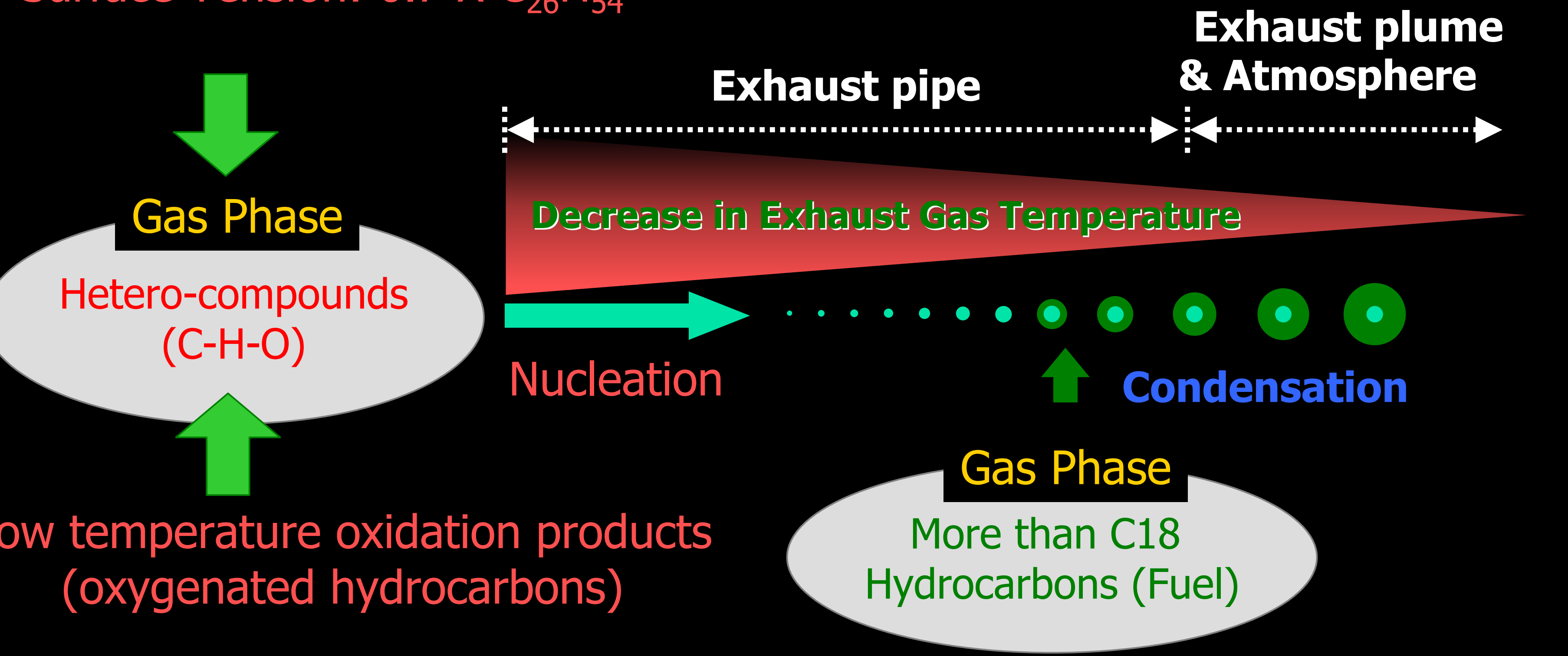
Analysis of Nucleation Particles at Idle

We analyzed nucleation particles to clarify some nucleation materials in the formation of nucleation particles at idle.

- Hydrocarbons of fuel or oil are observed in the whole diameter range and its percentage contents are independent of particle diameter.
- Hetero-compounds (low temperature oxidation HCs) exist in a high ratio in the range of nanoparticle diameter.
- These compounds have lower vapor pressure than high boiling point HCs in fuel ($C_{26}H_{54}$) have.
- Hetero-compounds would be nucleation material under idling condition.

Formation Mechanism of Nucleation Particles under Idling Condition

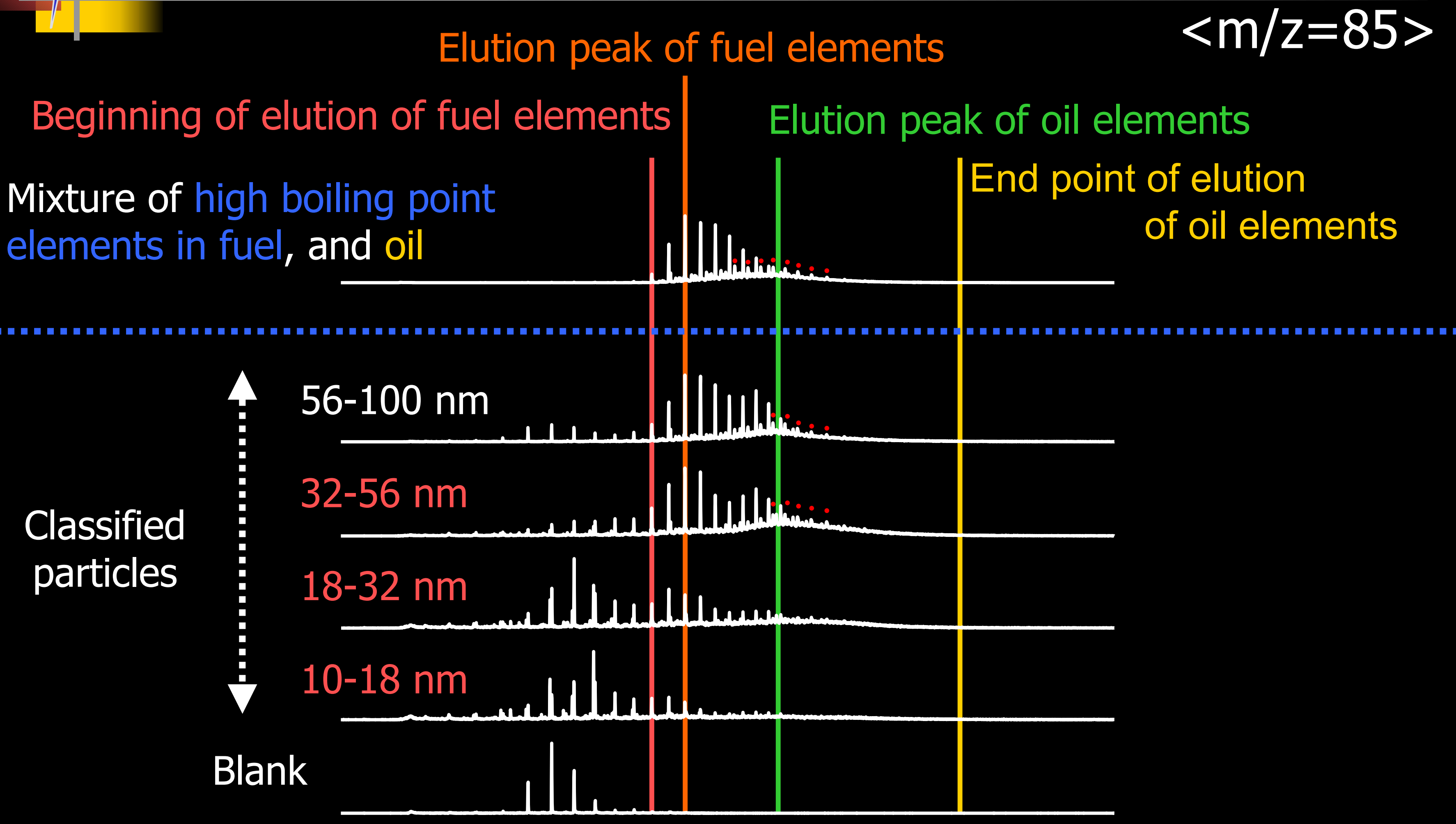
Vapor Pressure: 1/10,000 X $C_{26}H_{54}$
Surface Tension: 0.7 X $C_{26}H_{54}$



Main Components of nanoparticles at idle

Thank you very much
for your attention!!

GC-MS Analysis of Classified Particles 1



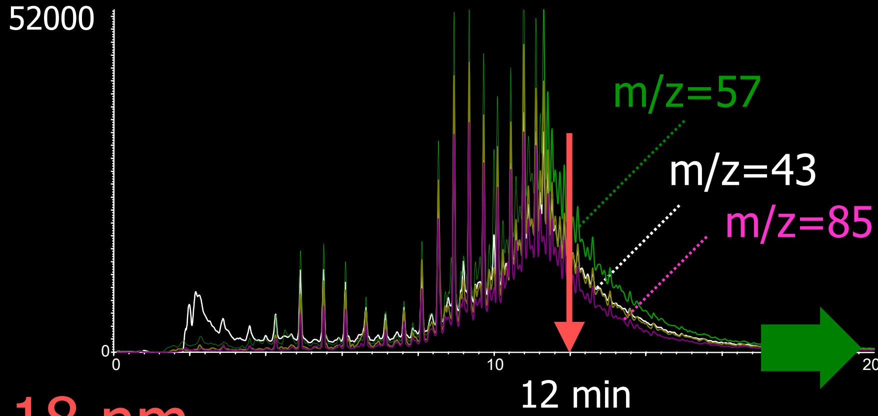
- Elements of fuel and oil exist in a whole range of particle diameter.

Comparison between m/z85 and m/z43

Mixture of high boiling point elements in fuel, and oil

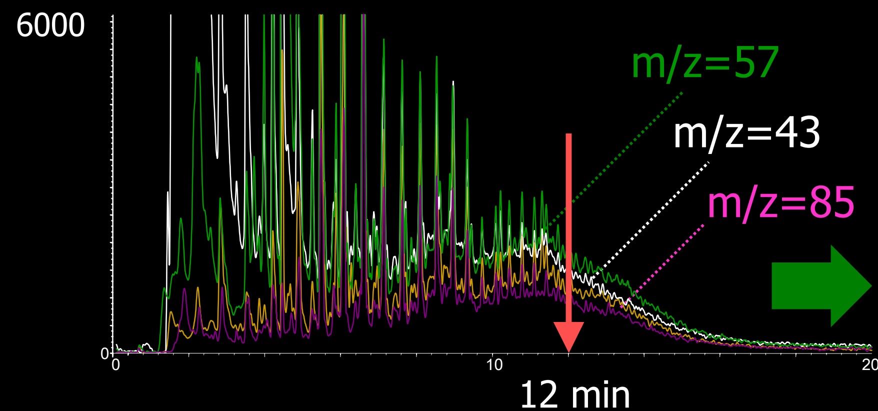
(m/z=85)/ (m/z=43)
=0.82 (12 min)

56-100 nm



(m/z=85)/ (m/z=43)
=0.70 (12 min)

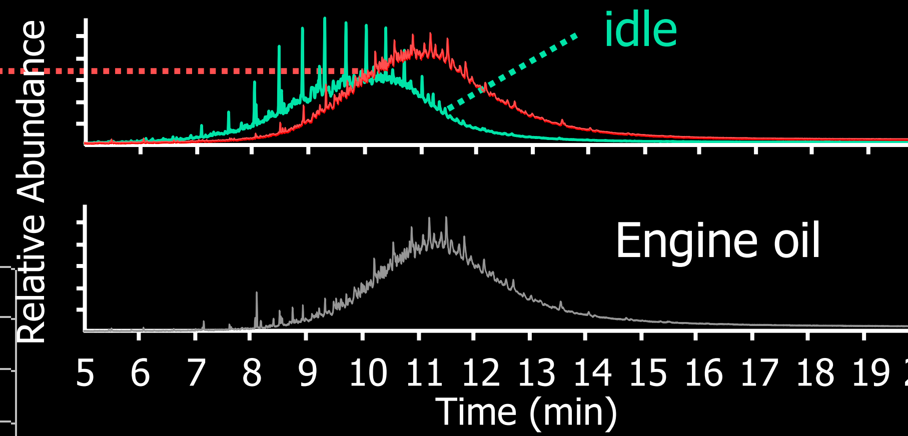
10-18 nm

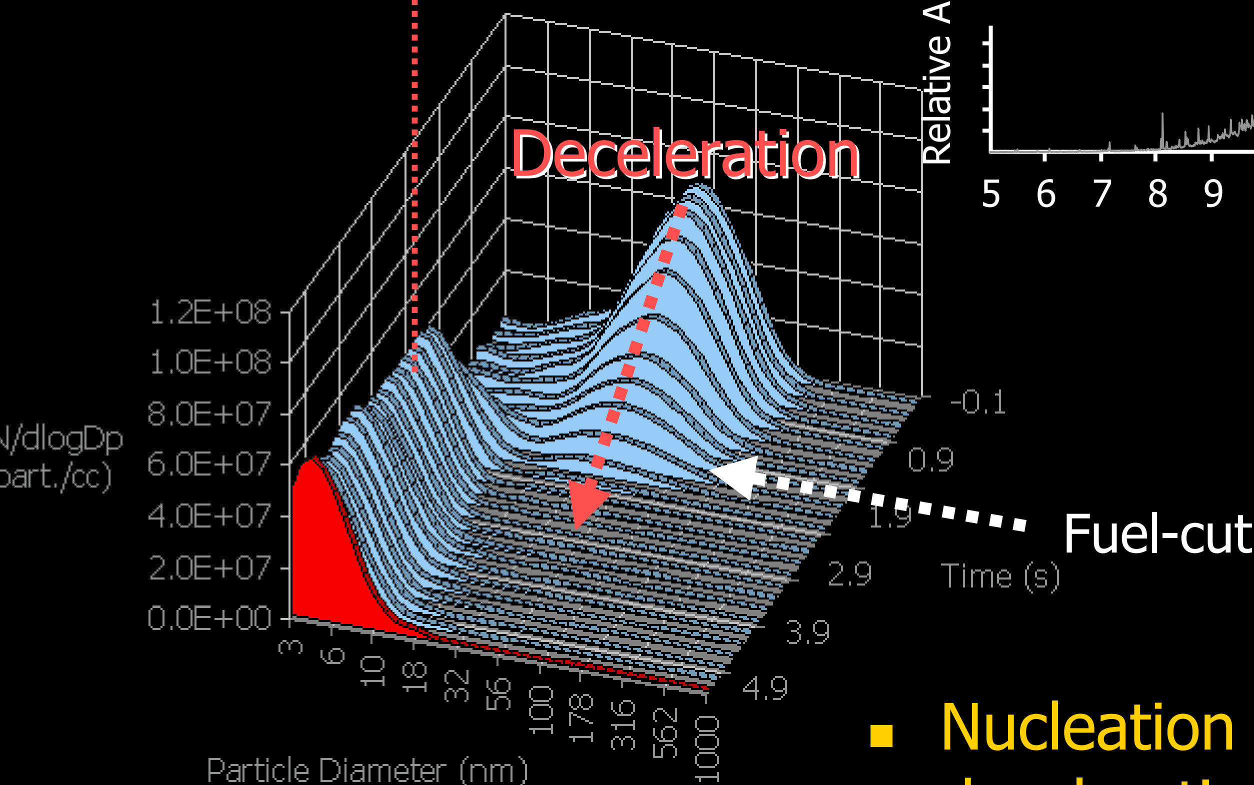


(m/z=85)/ (m/z=43)
=0.57 (12 min)

- This result suggests existence of heterocompounds (C-H-O) in the range of nanoparticle diameter.

Nucleation particles during Deceleration





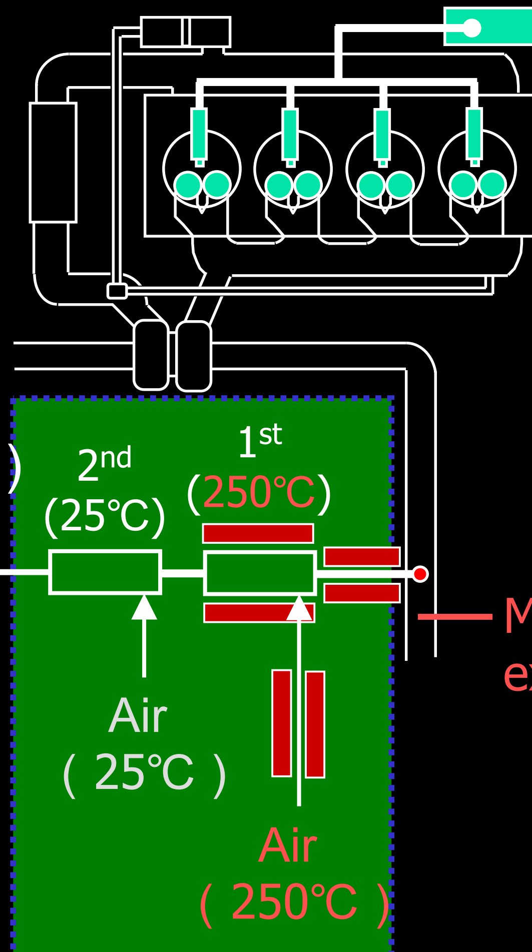
- Nucleation particles during deceleration are composed of engine oil elements.

Experimental Set-up for Transient Test

- Engine operating condition : 2500rpm-110Nm
  -> 2500rpm-Motoring
- Fuel : S=420ppm diesel fuel

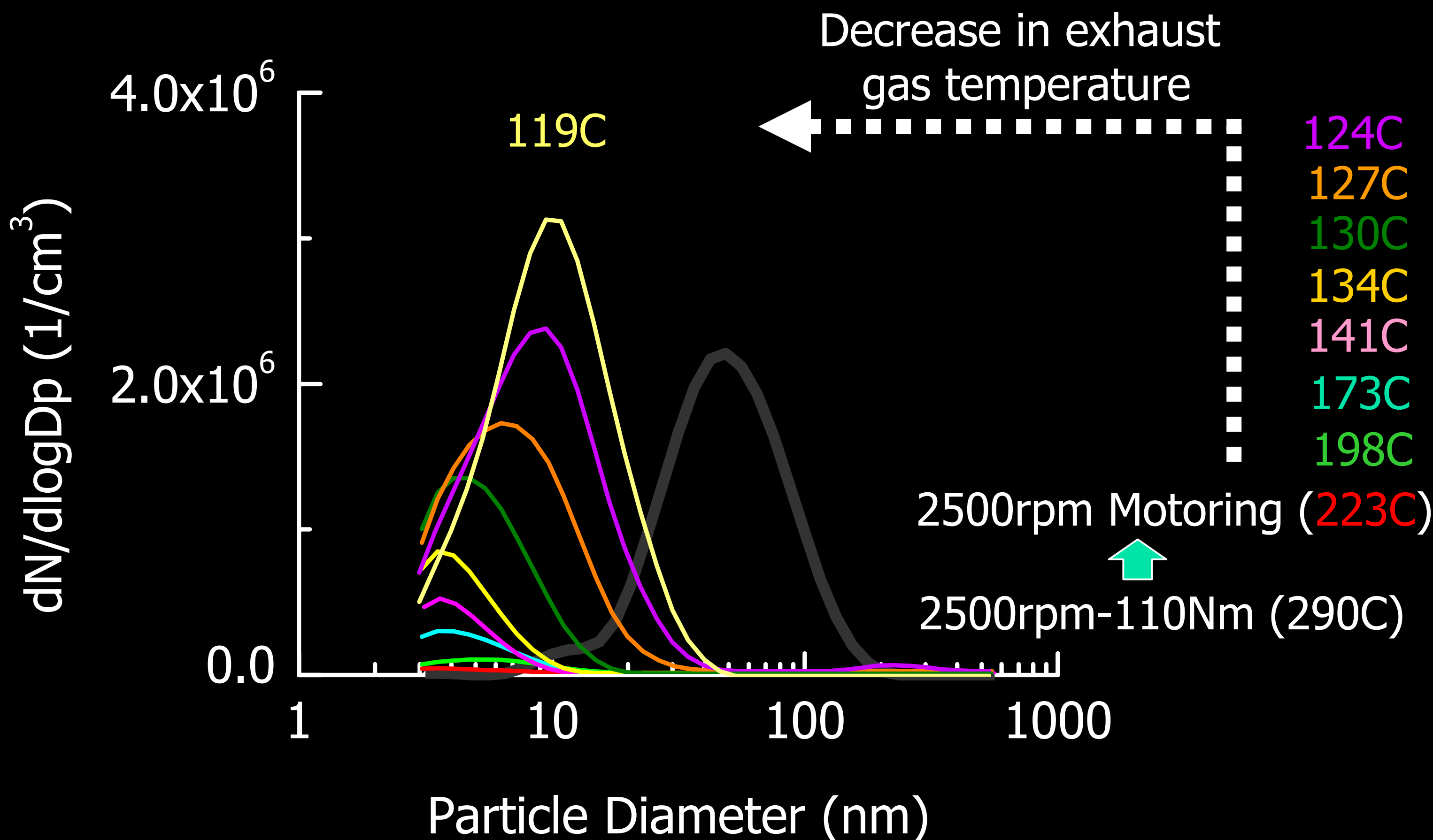
4-cylinder (2L)
DI diesel engine

DEKATI Dilutor
(Dilution ratio: 64)



Measurement of
exhaust gas temperature

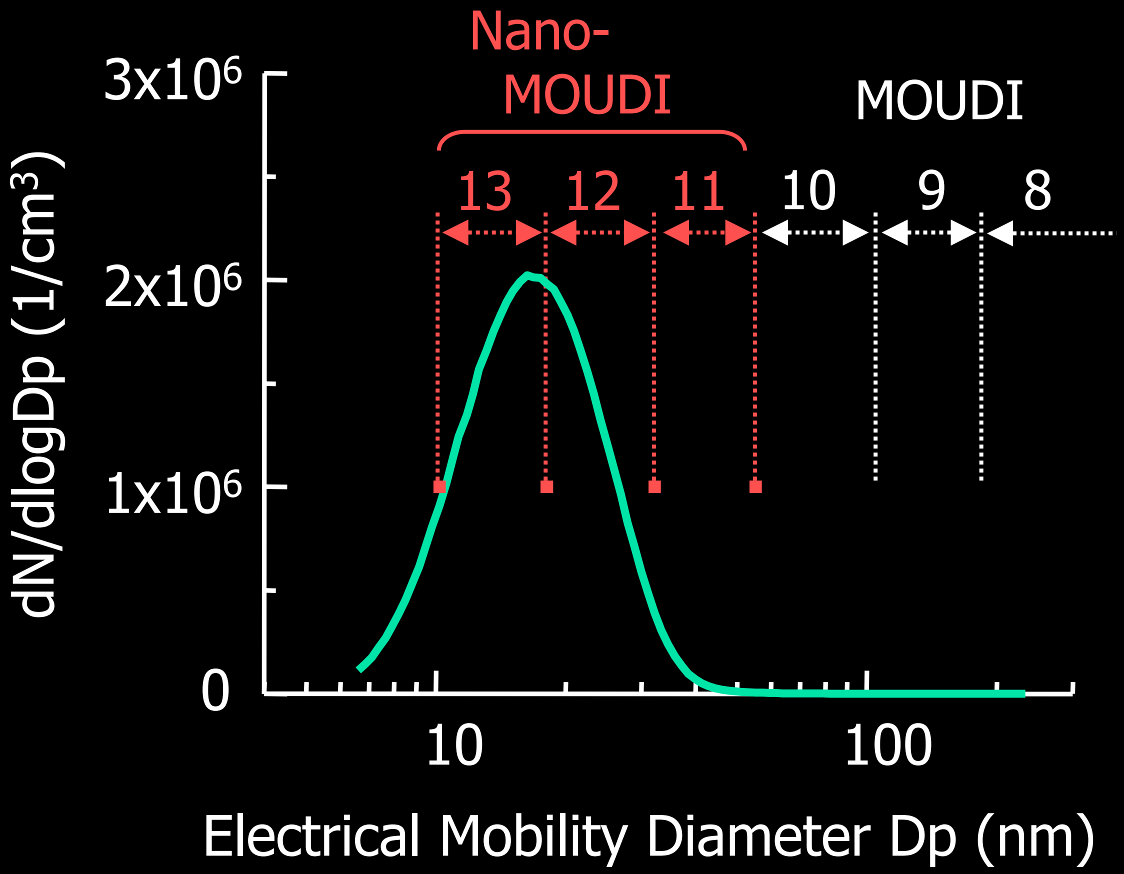
Formation of Nucleation Particles under deceleration condition



- Nucleation particles under deceleration condition also exist at more than 100 C of exhaust gas temperature.

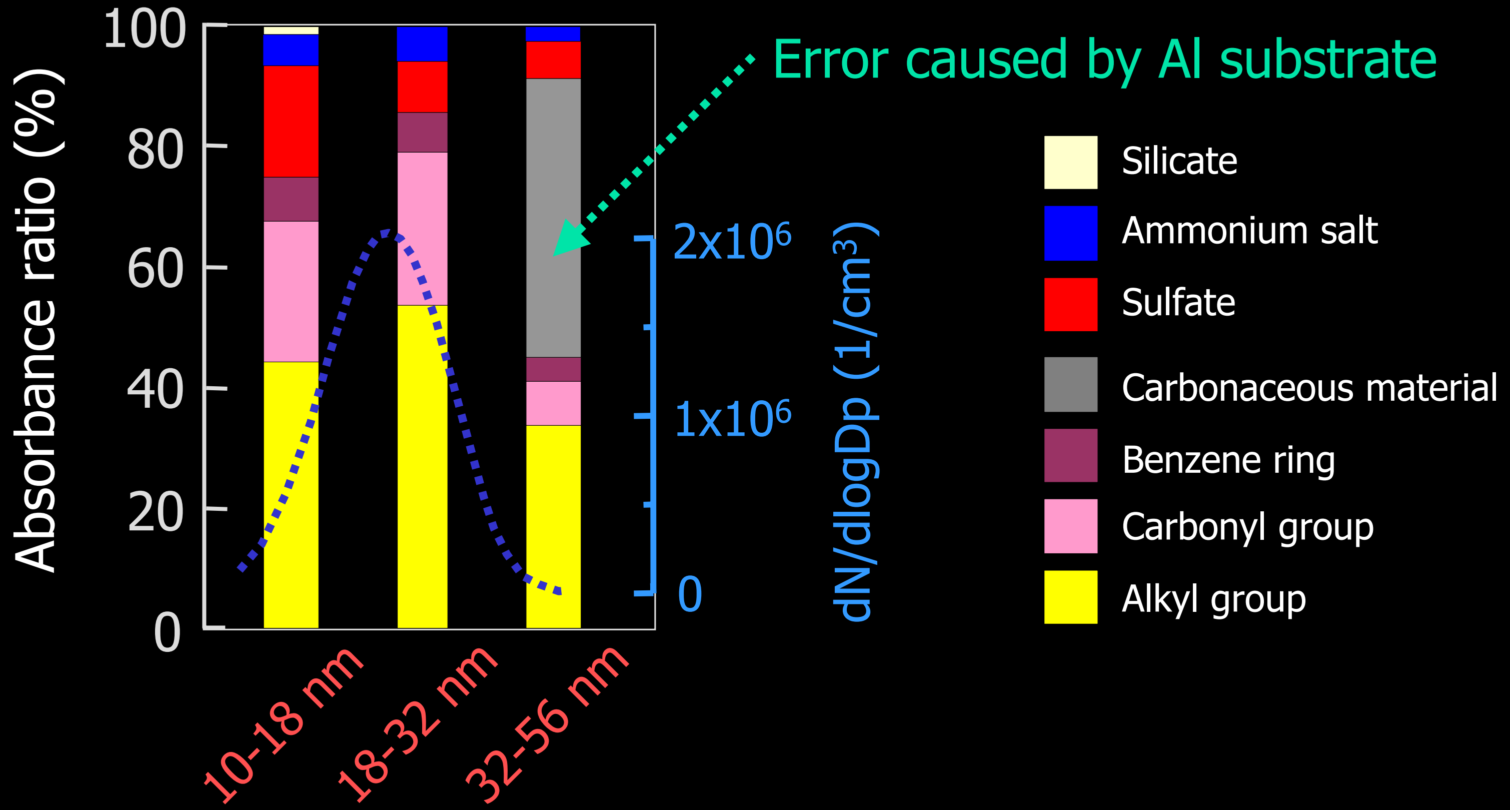
Particle Size Distribution during Motoring

1250rpm



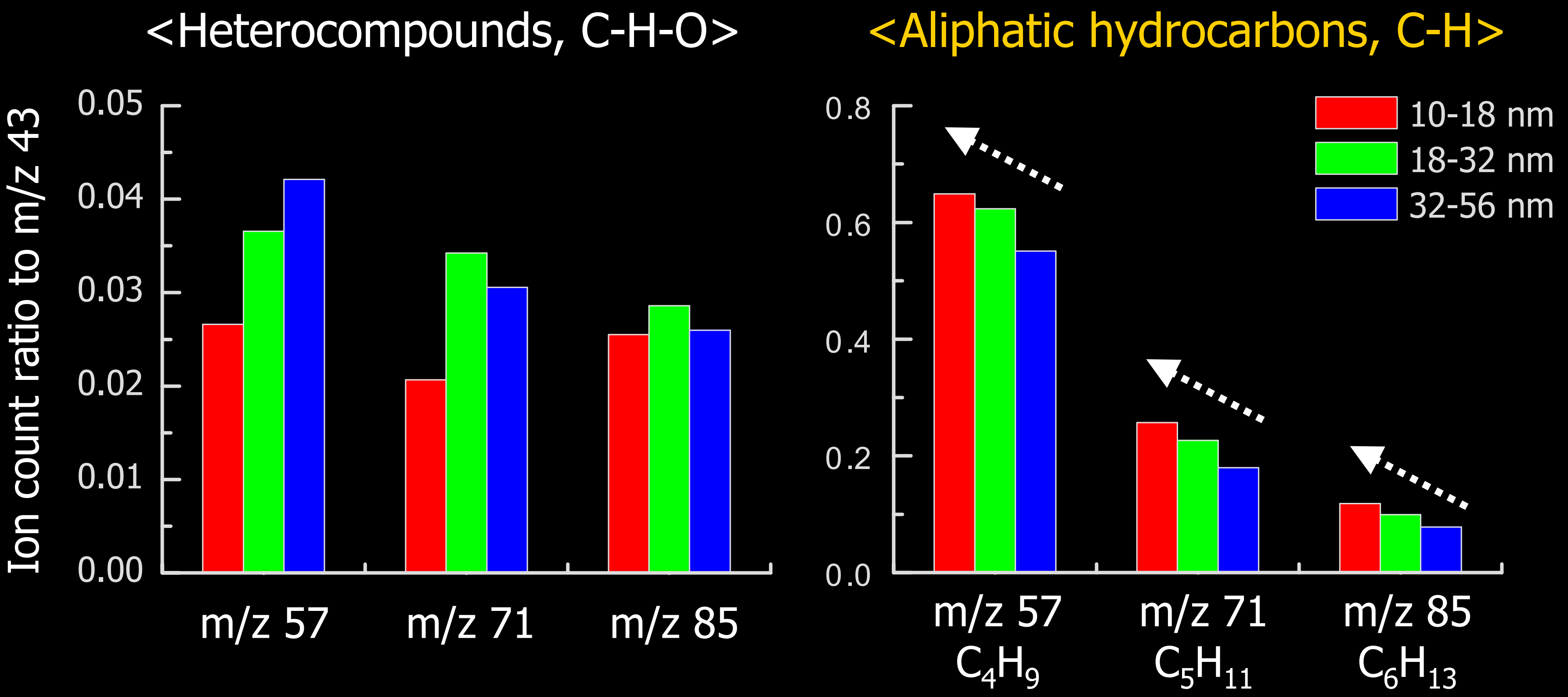
FT-IR Analysis of Nucleation Particles

Under Motoring Condition



- Hydrocarbons and oxygenated hydrocarbons are the main components of nucleation particles under motoring condition.

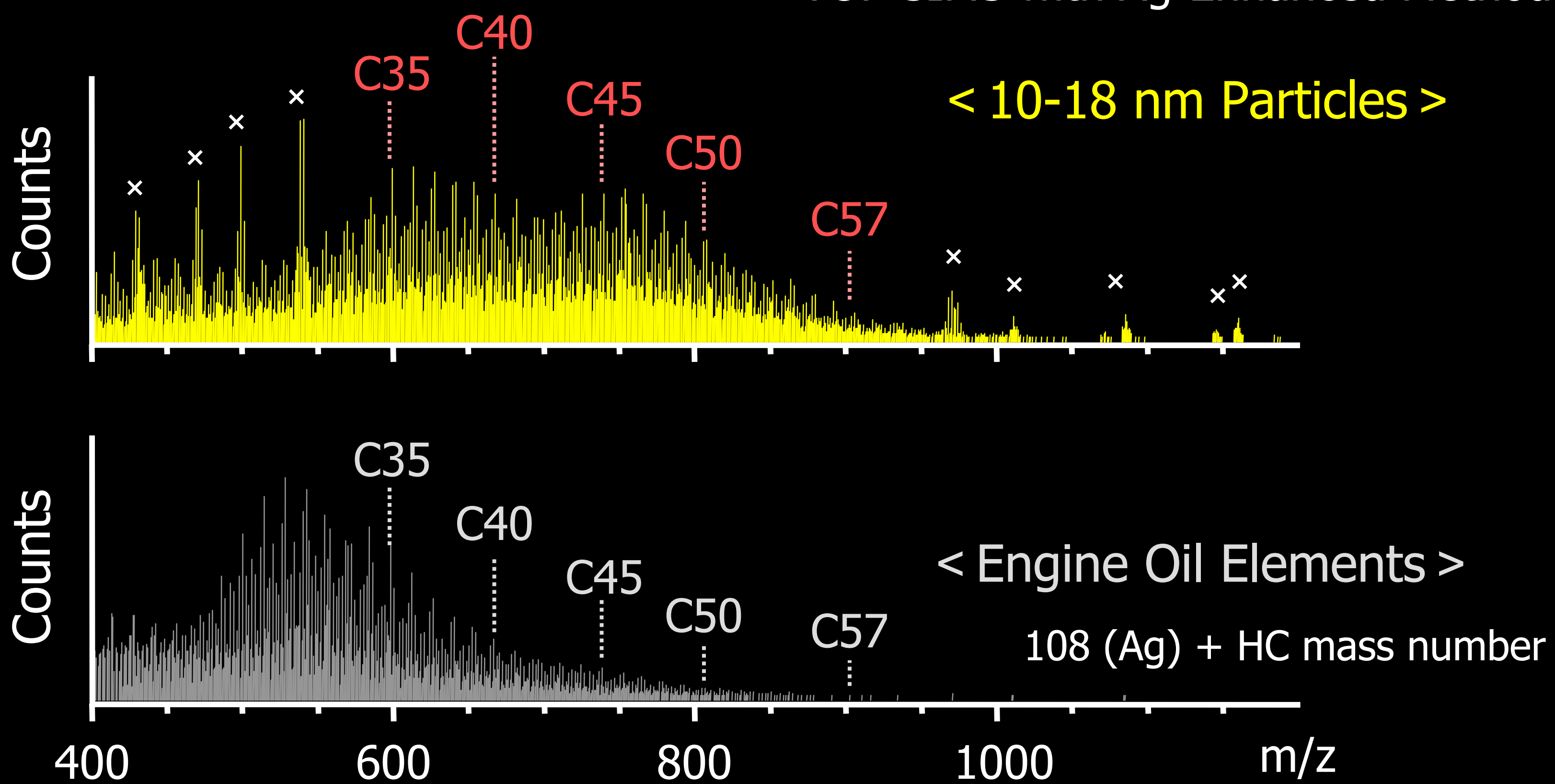
Nucleation Materials under Motoring 1



- The percentage content of aliphatic hydrocarbons increases with decrease in particle diameter in contrast to that of the hetero-compounds.

Nucleation Materials under Motoring 2

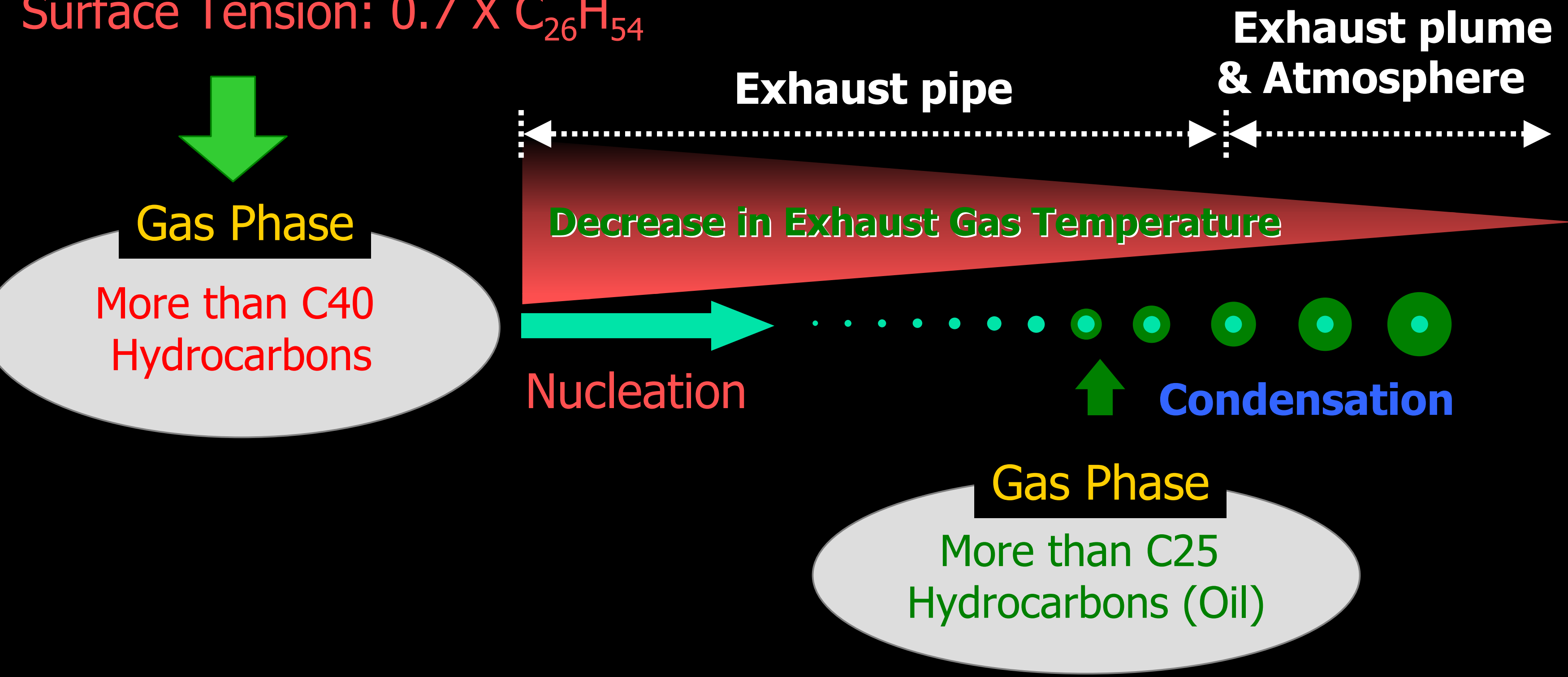
TOF-SIMS with Ag-Enhanced Method



- More than C40 paraffins of oil elements would be nucleation material under motoring condition (under deceleration condition).

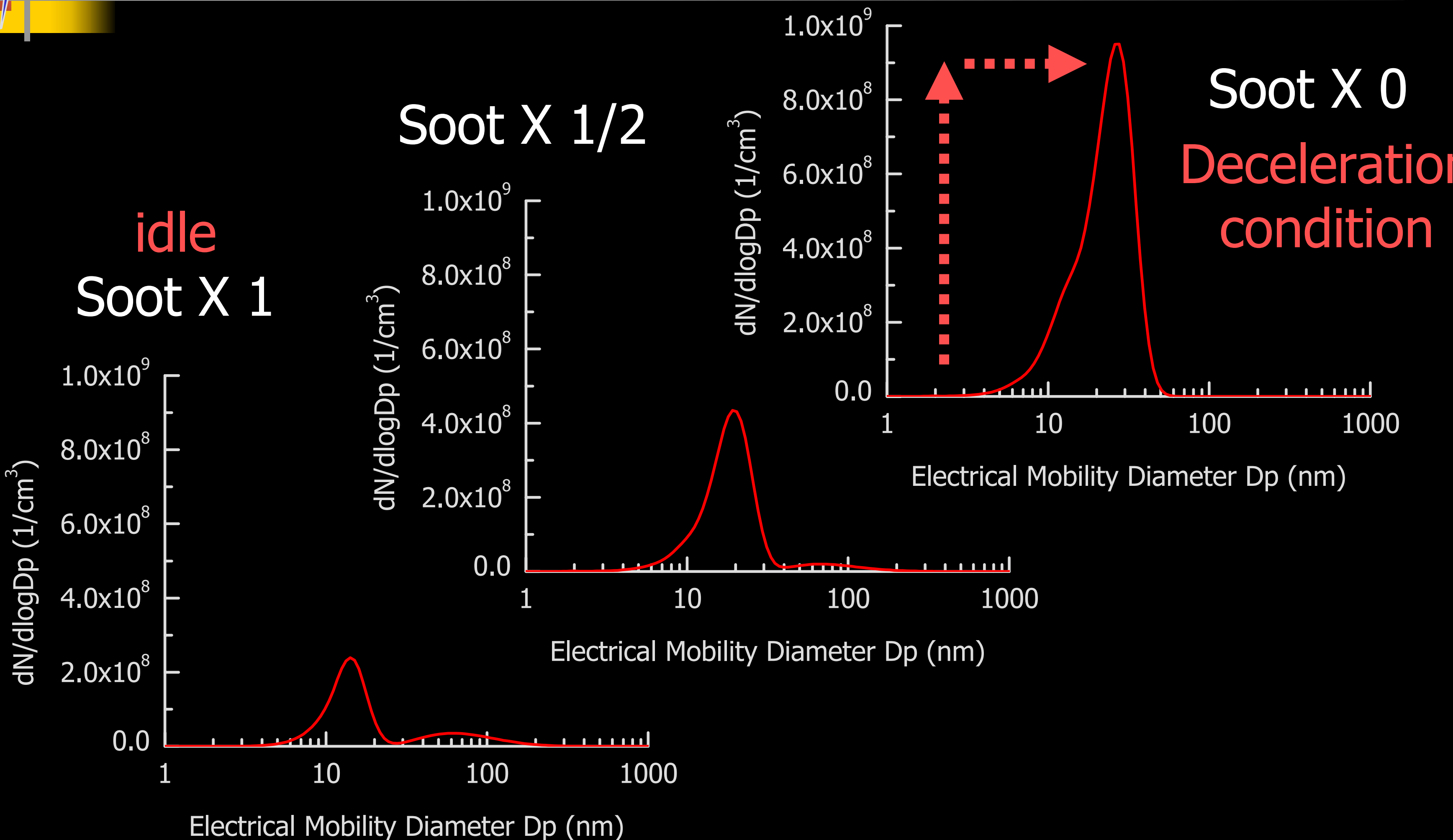
Formation Mechanism of Nucleation Particles under Deceleration Condition

Vapor Pressure: 1/10,000 X $C_{26}H_{54}$
Surface Tension: 0.7 X $C_{26}H_{54}$



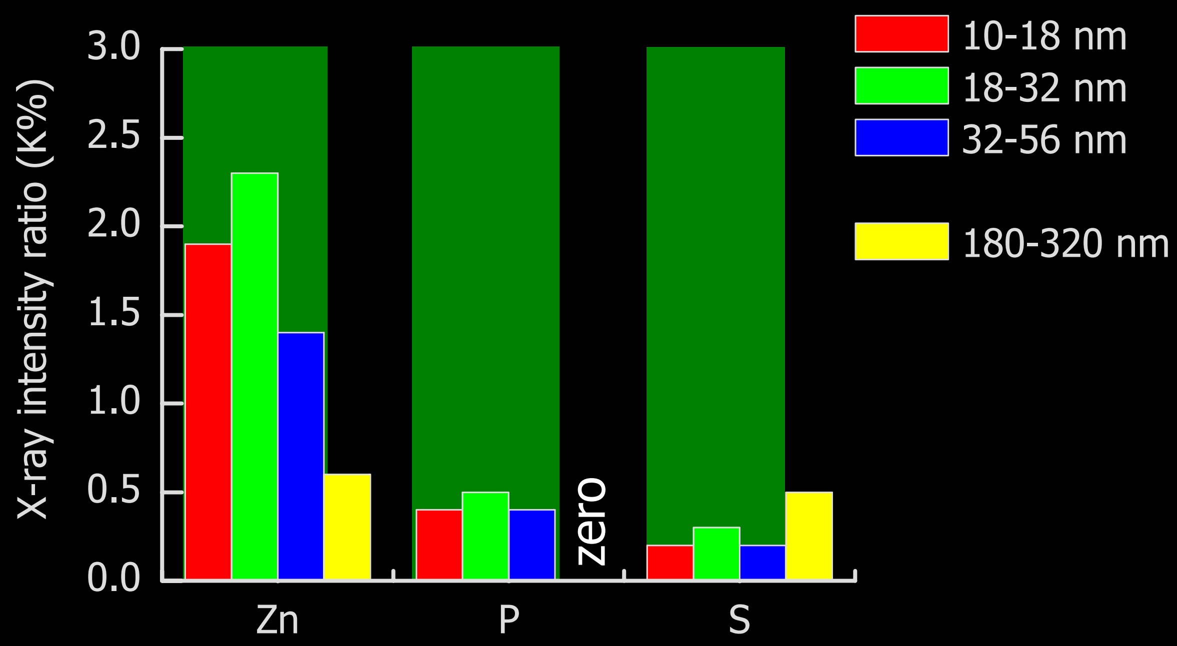
Main Components of nucleation particles under deceleration condition

Effect of Soot Number Concentration



- Suppression of soot causes increase in number concentration and diameter of volatile nanoparticles.

EPMA Analysis of Classified particles



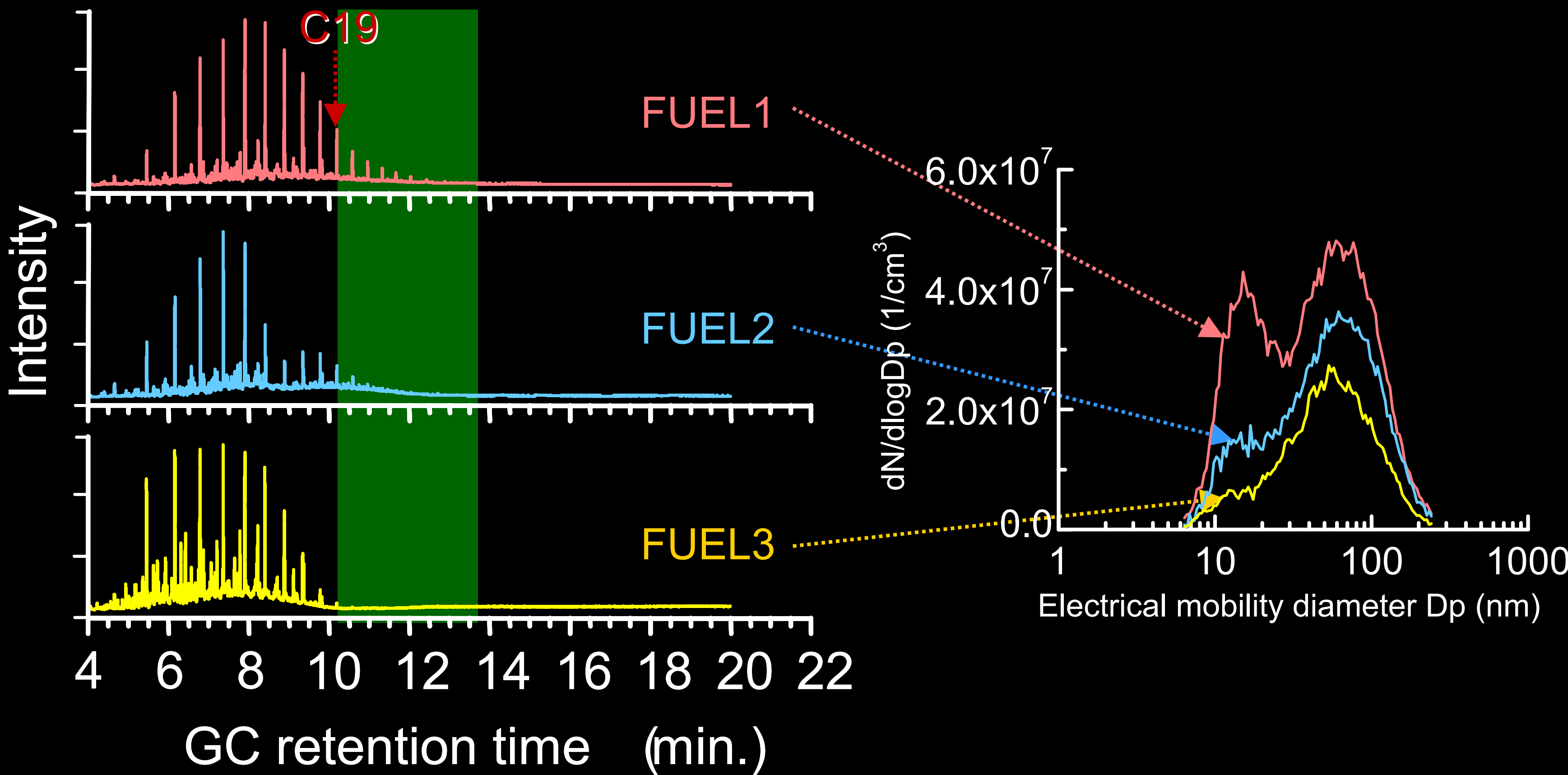
- Zn and P increase in the range of nanoparticle diameter
- EPMA data is in good agreement with TOF-SIMS data.

Introduction

We clarified three engine operating conditions where volatile nanoparticles were observed and main components of volatile nanoparticles exhausted from a light-duty diesel engine system.

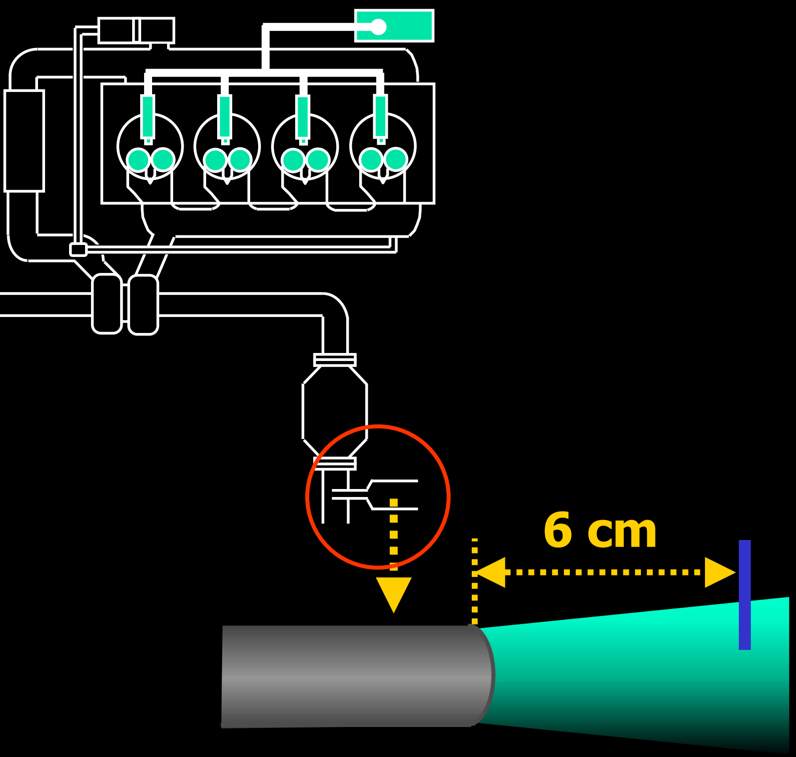
Engine Operating Conditions	Idle (non-load)	Deceleration	Mid- & Hi-load
Main Components	> C_{18} HCs	> C_{25} HCs	H_2SO_4
Source	Fuel	Oil	Sulfur compounds in fuel

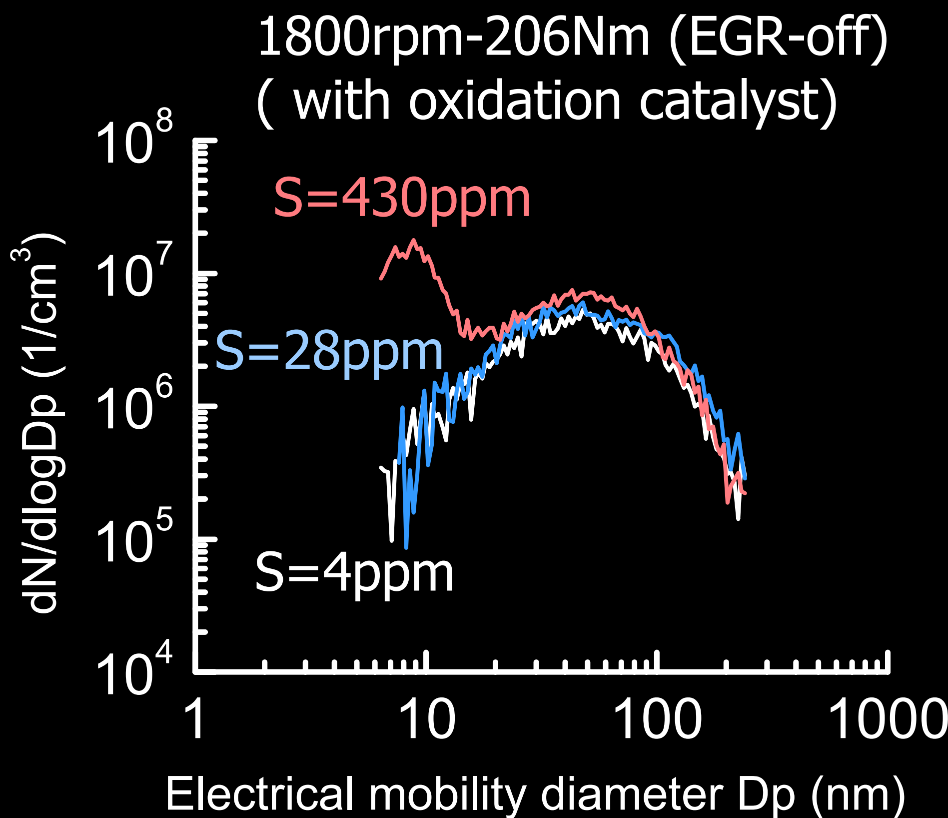
Nanoparticles at idle



- Nanoparticles at idle are composed of more than C18 hydrocarbons in fuel.

Nanoparticles under High Load Conditions





- Number concentration of nanoparticles depends on sulfur content in fuel. Nanoparticles under high load conditions consist of H_2SO_4 formed by SO_3 +nH_2O.

Objective & Method

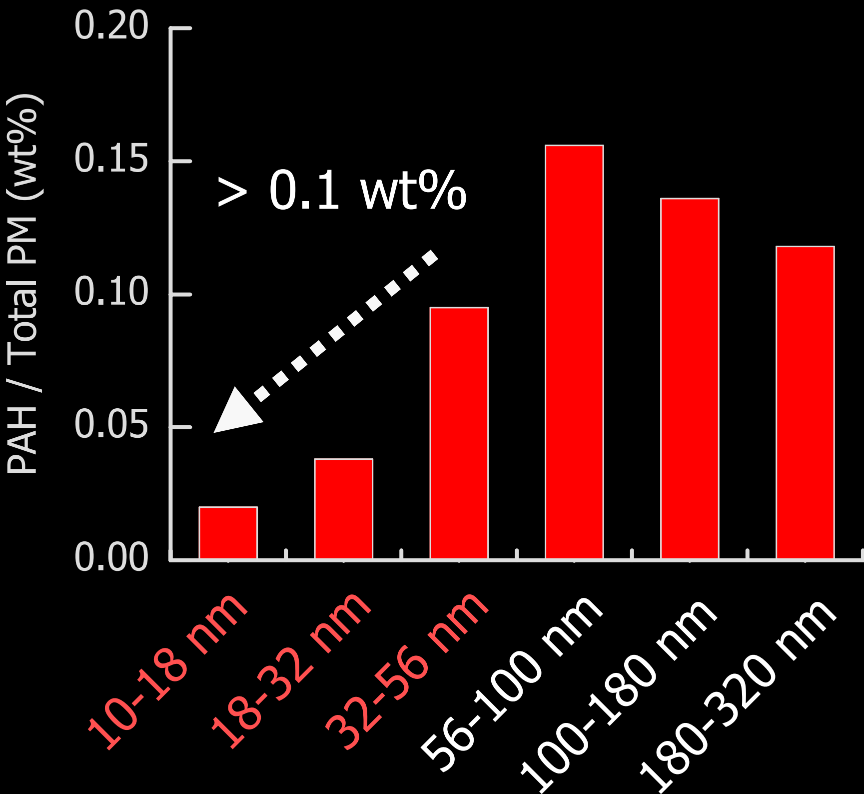
- To clarify some nucleation materials in formation of volatile nanoparticles at idle.

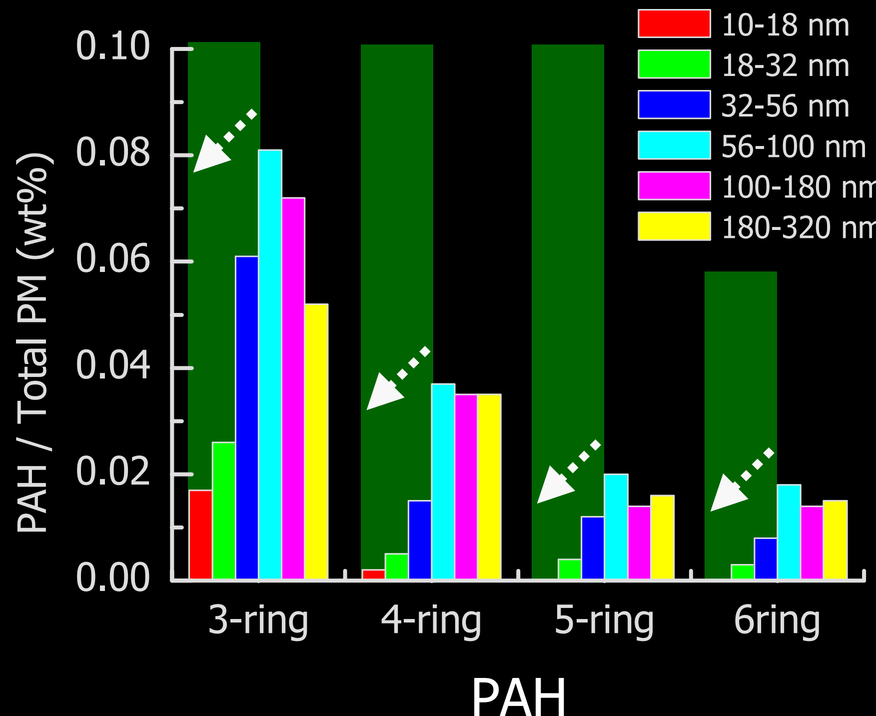
1. Particle sampling by using MOUDI & nano-MOUDL.

2. Analysis of classified particles (10nm-320nm) with EPMA, FT-IR, GC-MS and TOF-SIMS.

PAH Contents in Classified Particles

- GC-MS Analysis -





- PAH content decreases in the range of 10-56nm in diameter.