A New Dual-type DMA for the Measurement of Nanoparticles from Engines

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The differential mobility analyzer is the only practically applicable apparatus which can measure nanoparticle size distribution smaller than 300 nm in air. In the past, we have developed a DMA of which accuracy of the measurement was confirmed using fullerene C_{60} sublimated in the carrier gas as a new standard nanoparticle. A C_{60} monomer in the gas phase was produced by heating C_{60} powder under low-pressure conditions, and its mobility spectrum was observed using a low-pressure differential mobility analyzer. Pressure dependence for the C_{60} monomer in the spectrum was measured in order to examine the influence of C_{60} aggregates on the peak profile of the C_{60} monomer. Taking into account the diameter of the collision partner Ar atom, the diameter of the C_{60} monomer was estimated in the framework of Stokes' law. This DMA is also sensitive enough to identify the geometric isomer of an observed C_{60} dimer.

However, generally speaking, conventional DMAs are not suitable to detect the transient behavior of nanoparticles from engines because the required voltage scanning time is relatively long (typically a few minutes).

Therefore, in order to detect the transient behavior of airborne nanoparticles with diameters of both ~ 10 nm and ~ 100 nm in automobile exhaust gas, a new dual-type differential mobility analyzer (dual-type DMA) has been developed.

In this dual-type DMA, the gas sample is divided into two parts, with each part being introduced into two respective coaxially nested sections for analysis. The nanoparticles are charged by ^{241}Am and their size distributions in the vicinities of 10 nm and 100 nm are then measured by scanning the applied voltage within 2 min (scanning mode measurement). In the transient mode measurement, on the other hand, the voltages for the two sections are fixed at peaks near 10 nm and 100 nm in order to monitor the transient behavior of the automobile exhaust's nanoparticles.

In the first experiment, we produced airborne model nanoparticles with a bimodal size-distribution when we mixed the NaCl nanoparticles (~10nm) produced by the sublimation-condensation method with the fume nanoparticles from burnt incense (~100nm). When the corona charger for the charging of the nanoparticles was switched on and off, the transient behavior of the dual-type DMA was studied.

In the second experiment, the exhaust gas from a diesel engine was introduced into the dual-type DMA and the transient behaviors of nanoparticles in the nuclei mode and in the accumulation mode were successfully detected by the dual-type DMA.

The measurement principles and the design of the dual-type DMA are thus explained together with experimental data regarding its resolution, sensitivity, and time response using both model nanoparticles and real nanoparticles in automobile exhaust.

In conclusion, it was shown that the dual-type DMA is simple, robust and capable to become the standard apparatus for the measurement of airborne nanoparticles from engines.

1) H. Tanaka and K. Takeuchi: “C_{60} Monomer as an Inherently Monodisperse Standard Nanoparticles in the 1nm Range”, Jpn. J. Appl. Phys., 41, 922(2002).
2) H. Tanaka and K. Takeuchi: “Structure Identification of a C_{60} Dimer Using Electrical Mobility Measurement”, Jpn J. Appl. Phys., 43, 7A, 4462(2004).
3) H. Tanaka and K. Takeuchi: “Experimental Transfer Function for a Low-pressure Differential Mobility Analyzer by Use of a Monodisperse C_{60} Monomer”, J. Aerosol Sci., 34, 9, 1167(2003).

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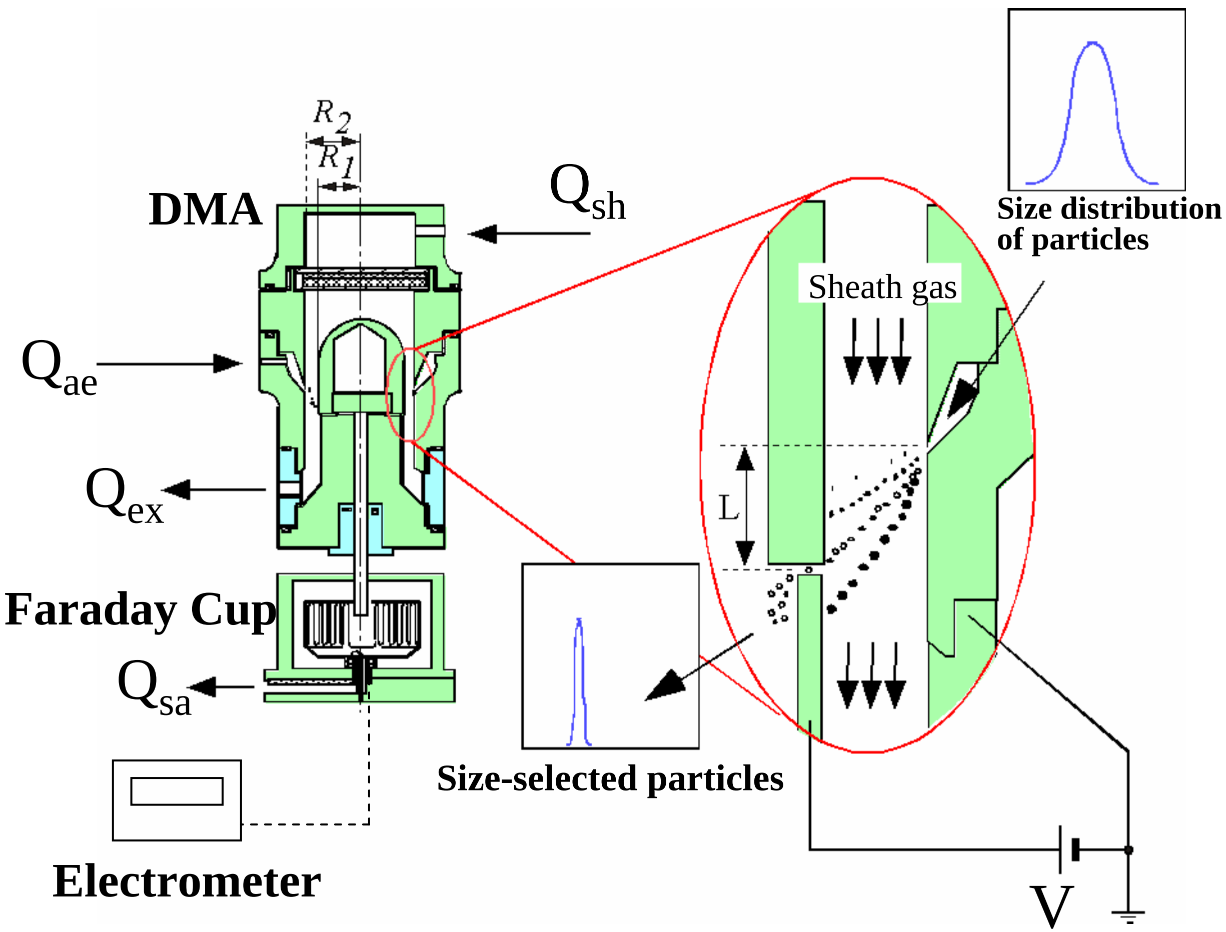
1. Measurement of Gas-borne Nanoparticles
2. Calibration of Size Measurement
3. Difficulties in Conventional DMAs
4. Dual-type DMA as a Solution
5. Experiment
6. Conclusion

Measurement of Air-Borne Nanoparticles

Nanoparticles: 1 nm < d_p < 300 nm

method	in-situ?	problems
TEM measurement after collection	no	• tedious procedure that requires preservation of the size distribution
light scattering	yes	• scattered light intensity $\propto d_p^6$ • not practically applicable to nanoparticles
mobility measurement using DMA	(yes)	• sensitivity and stability (historically). • calibration method below 10 nm.

Differential Mobility Analyzer (DMA)



Electrical mobility of particles

$$Z^* = \frac{Q_{sh}\ln(R_2/R_1)}{2\pi LV}$$

$$= \frac{n_p e C_c}{3\pi\mu D_p}$$

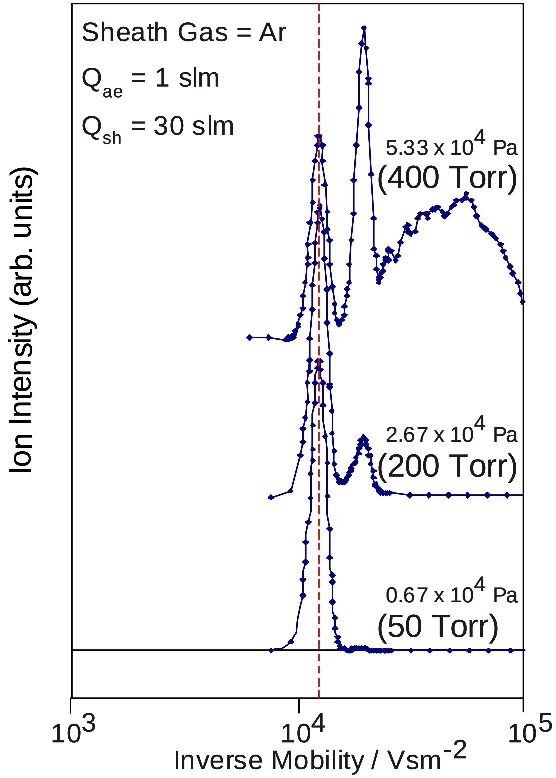
D_p: Particle diameter

C_c: Cunningham correction factor

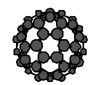
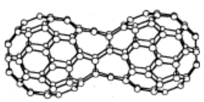
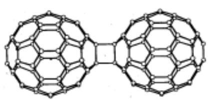
μ: Gas viscosity

n_p: Number of elementary charges on a particle

Size-selection of nanoparticles using DMA



Pressure Dependence of Mobilities for C_{60} and C_{60} Oligomers

geometry	isomer	experimental (this work) Vsm^{-2}	theoretical Vsm^{-2}
	C_{60}	2410	2424
	Peanut 56/56 $(C_{60})_2$		4054
	[2+2] 66/66 $(C_{60})_2$	4230	4227
	5-6 stick $(C_{60})_2$		4409

Strout *et al.*, *Chem. Phys. Lett.* **214**, 576 (1993).

Shvartsburg *et al.*, *J. Phys. Chem. A* **101**, 1684 (1997).

Calculated Mobilities for C_{60} and C_{60} Dimer

Problem for Conventional DMAs in Automobile Exhaust Measurement

Typically, conventional DMAs need to scan the voltage for 2 minutes

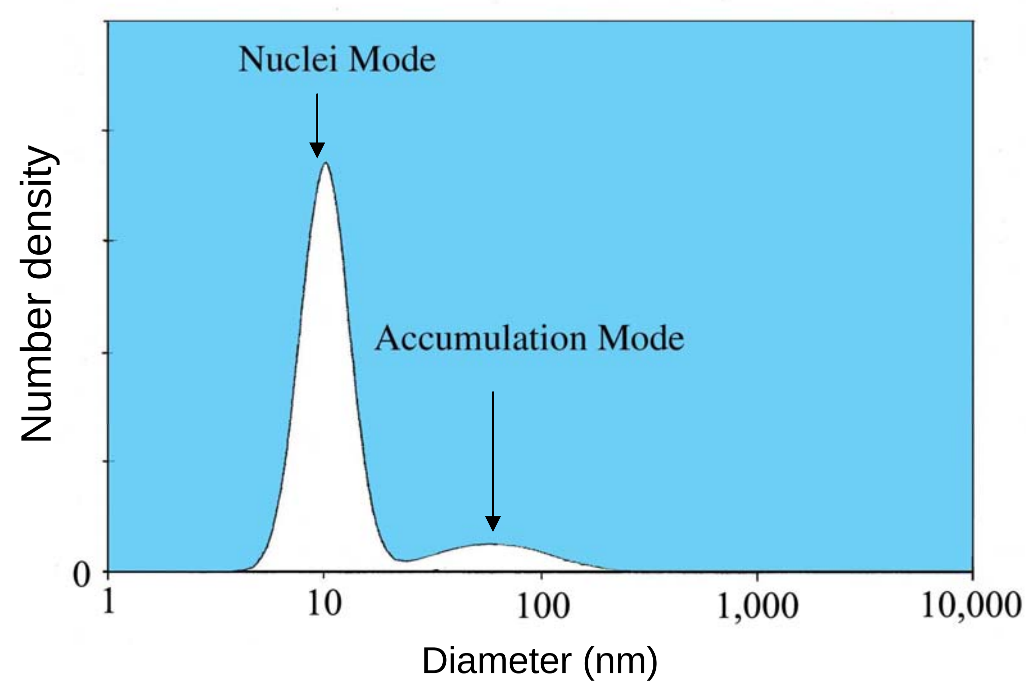
↓

Cannot cope with the quick transient behaviors in automobile exhaust

↓

DMA with a multi-channel detector

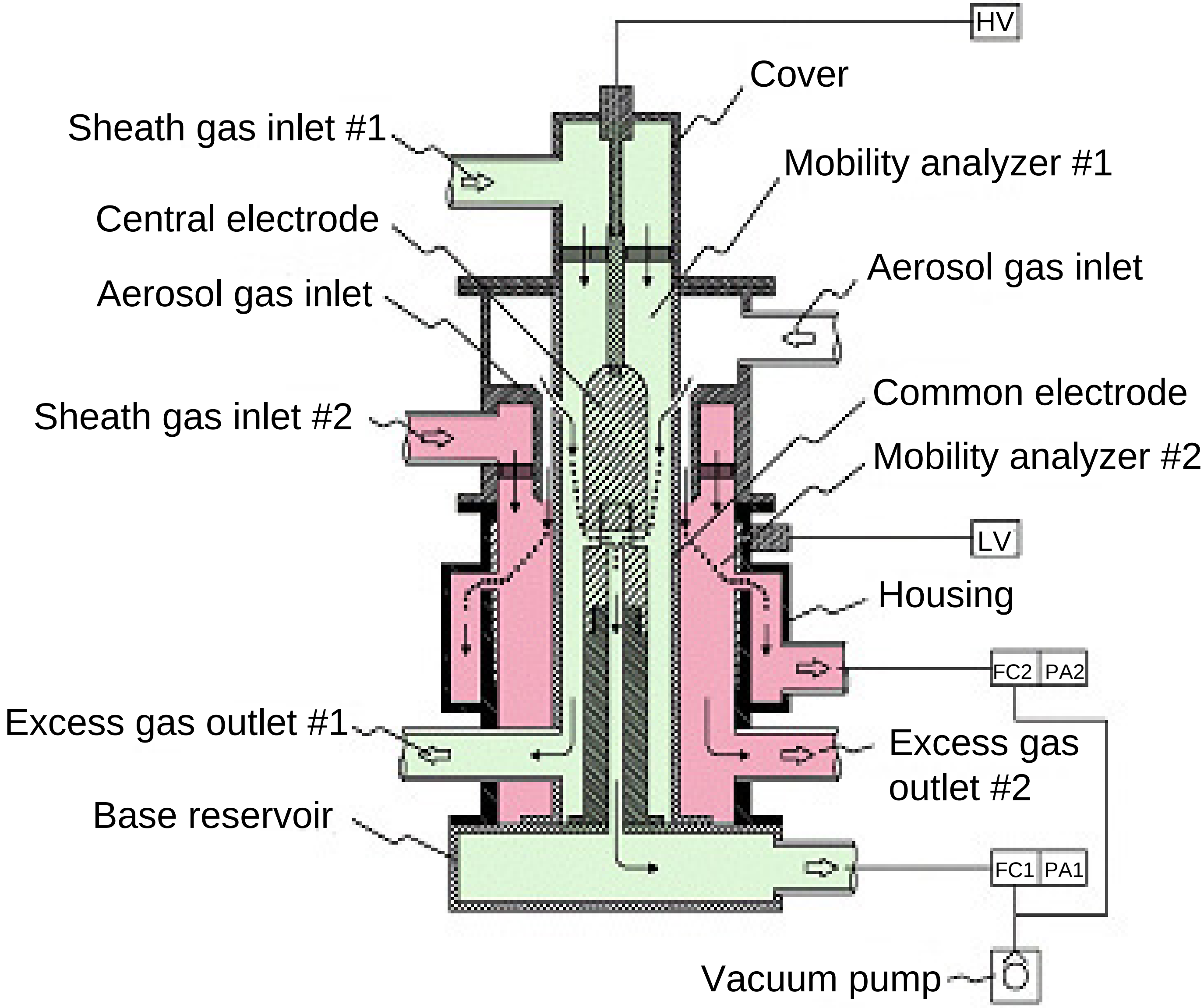
dual-type DMA with both
- scanning measurement mode and
- transient measurement mode



Typical particle size distribution of nanoparticles in engine exhaust

Image reproduced from
D.B. Kittelson and W. Watts,
Third Joint ESF-NSF Symposium Abs.,
Dublin, Sept. 6 (2000).

Dual-type DMA of Wyckoff



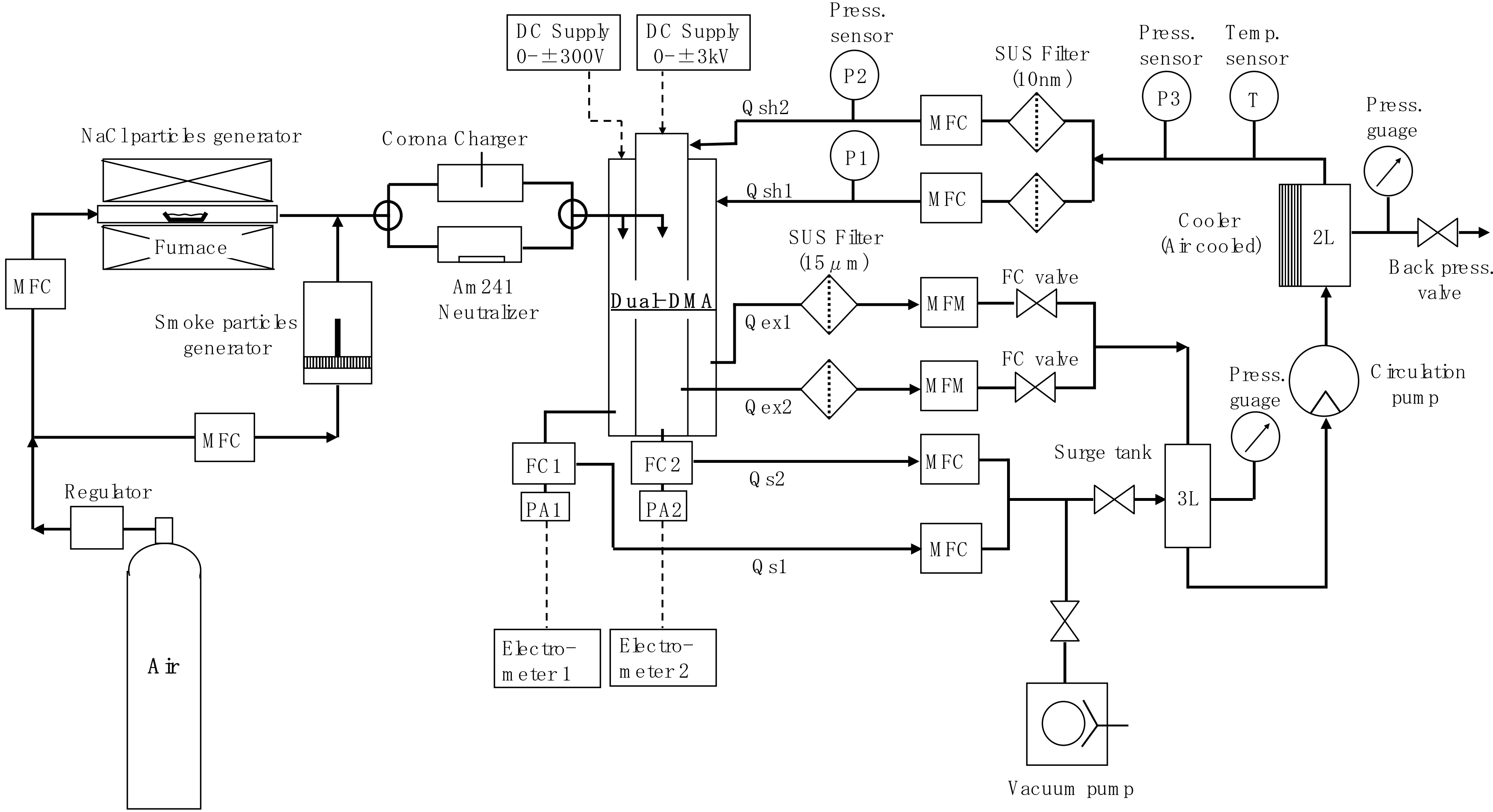
Features of the Dual-type DMA (DDMA)

1) The DDMA can be operated both in scanning measurement mode and in transient measurement mode.

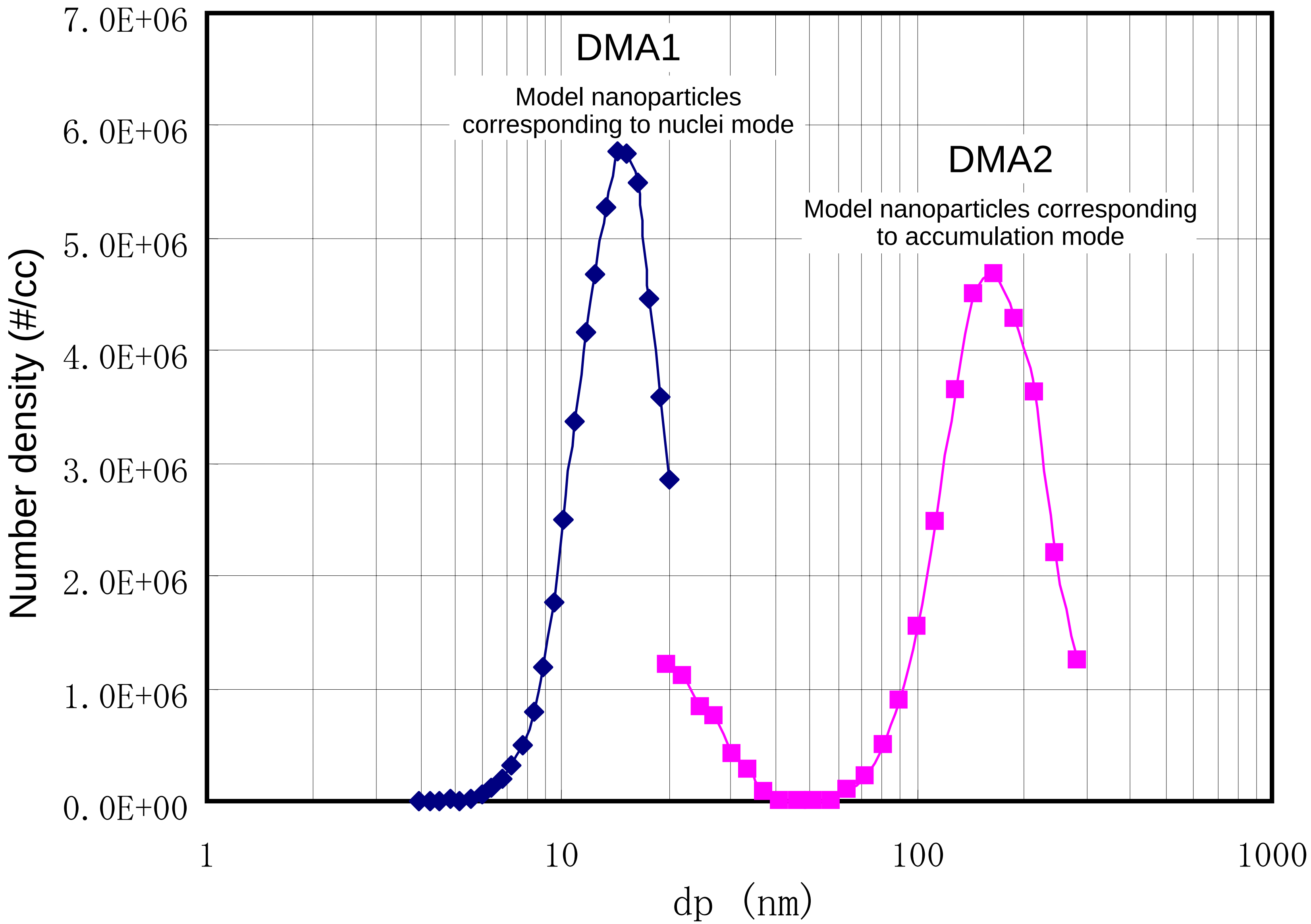
2) In transient measurement mode, voltages are fixed at the peak values of the nuclei mode and the accumulation mode.

3) Particle number density can be obtained by assuming that the shape of the size distribution is unchanged.

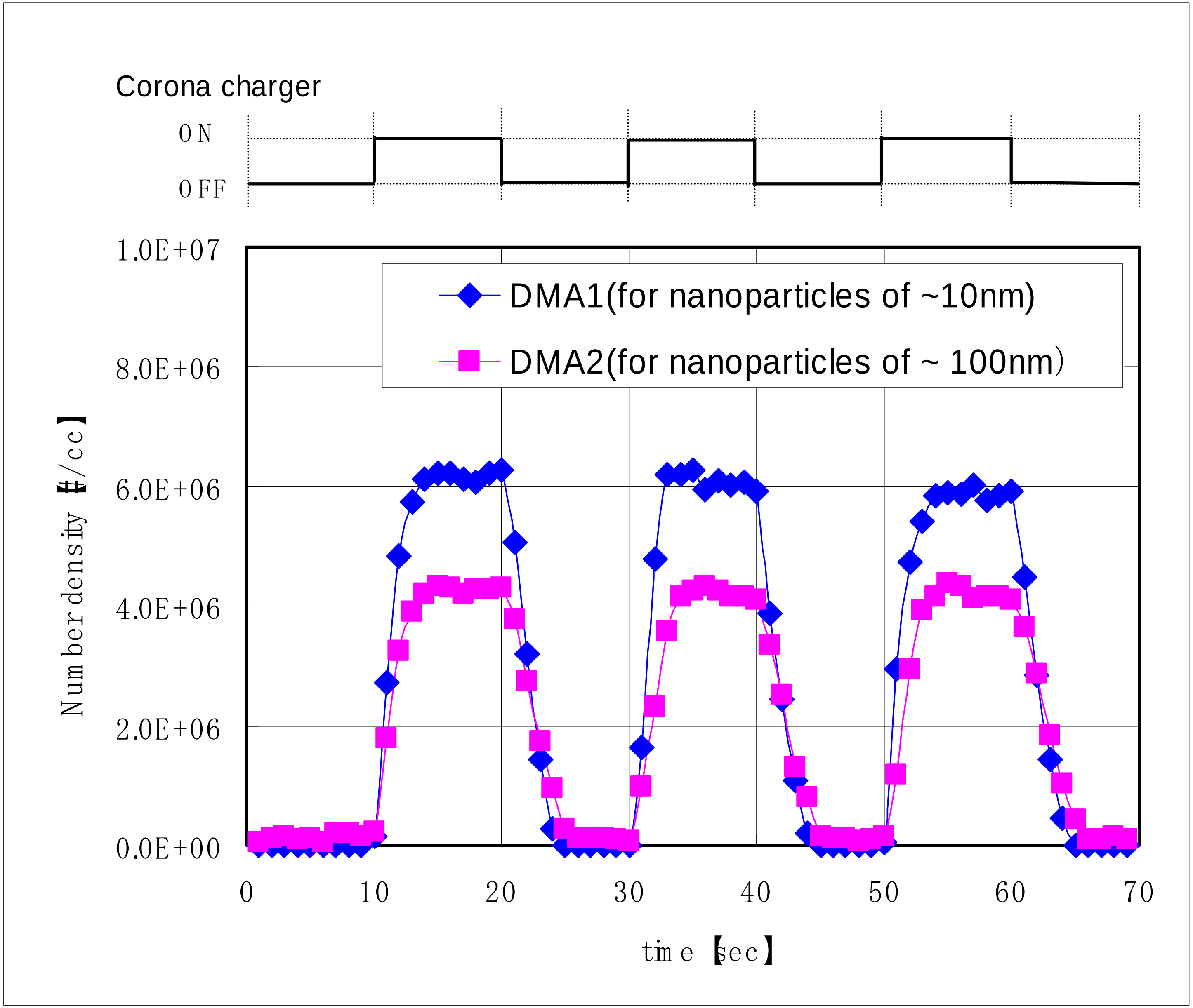
4) DDMA can be operated with intentionally reduced resolution.



Generation of model nanoparticles with bimodal size distribution

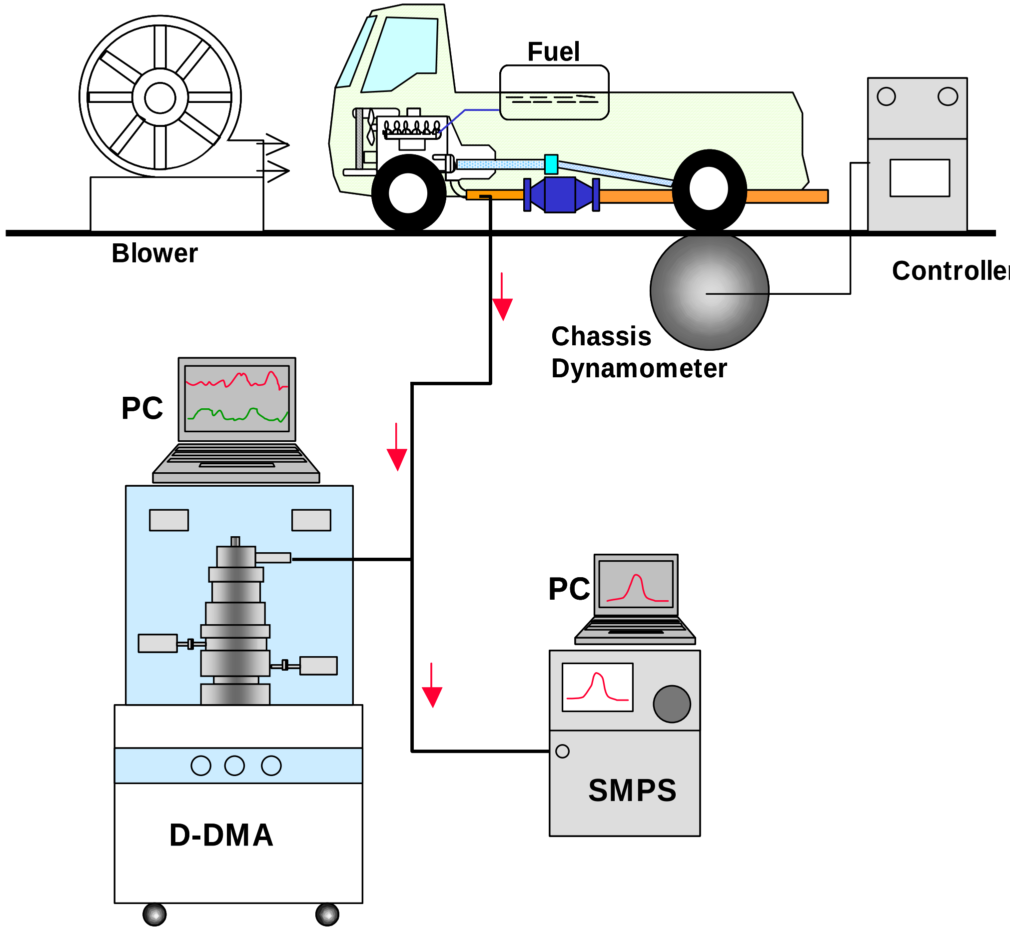


Scanning Mode Measurement of Model Nanoparticles



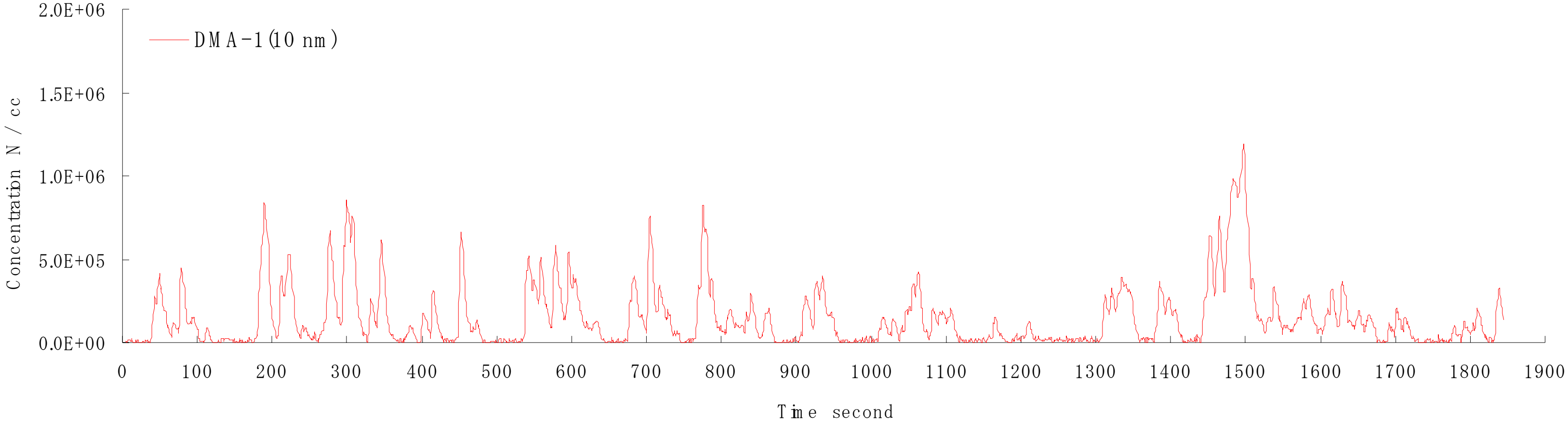
Transient Mode Measurement of Model Nanoparticles

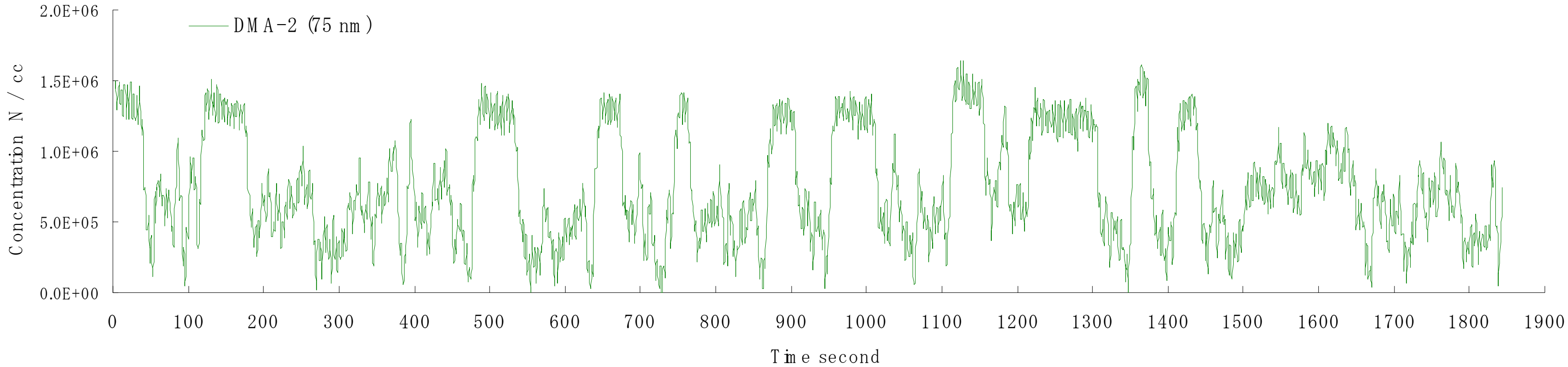
System Schematic

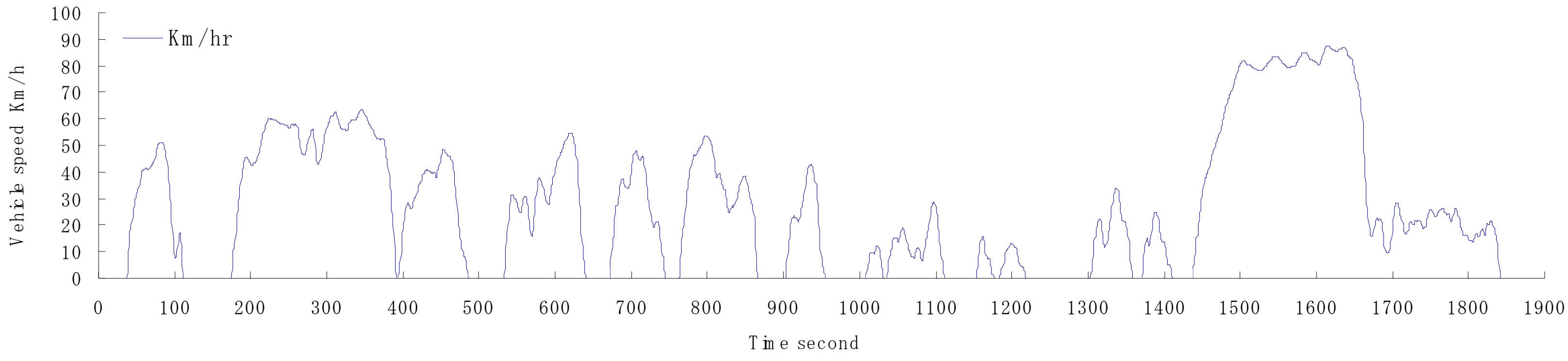


Measurement of nanoparticles from a Automobile Engine

Result for JE-05 Driving Mode







Concluding Remarks

1) We have introduced the dual-type DMA (DDMA) of Wyckoff.

2) The DDMA is simple and robust, and would be easy to use as a standard apparatus for the measurement of nanoparticles in automobile exhaust.

3) At the completion of this project, Shimadzu Co. will commercialize the DDMA and will be capable of large-scale production.

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