

Measurement of Diesel Solid Nanoparticle Emissions

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Introduction

The current gravimetric methods used for the legal determination of emissions have difficulty accurately quantifying Particulate Matter (PM) mass emissions as regulations continue to get more stringent. Although the US EPA issued an improved protocol for the current gravimetric method, accuracy will continue to be an issue at a very low level emission from new vehicles. The European Particle Measurement Programme (PMP) is a particle measurement protocol which aims to measure solid particle number emissions. The PMP protocol specifies measurement of particles larger than 23 nm, to exclude the possible measurement artifact caused by volatile particles present in nucleation mode. It is a promising method to possibly complement regulatory mass measurements. The PMP protocol is included in Euro 5/6 proposed emission regulations. The proposed number emission limit of 6×10^{11} particles/km would be applicable to all categories of light-duty diesel vehicles at the Euro 5 and Euro 6 stages.

The potential of PMP protocol for heavy-duty vehicles/ engines has been recently studied in Europe and the United States. During CARB's previous studies on PMP, we found there are significant number of appeared-to-be solid sub-23nm particles that can make it past the PMP volatile particle remover [1]. It is very important to find out whether these operationally determined solid particles are real solid particles (such as partially burned soot or ash) less than 23nm or low-volatile compounds and to compare particle emissions during cycles and real world on-road driving as either case will suggest modification of the PMP method.

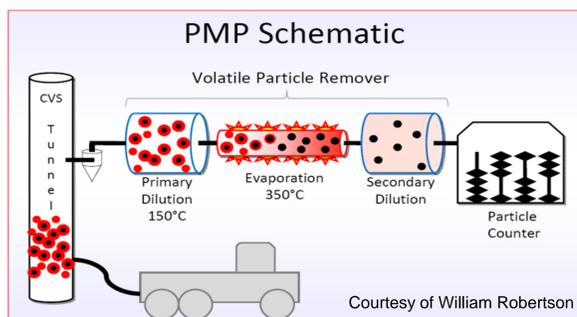
A Catalytic Stripper (CS) consists of two catalysts that convert the diluted exhaust gas components as well as volatile species on the surface of the particles. One catalyst is responsible for absorbing sulfur components and the other removes all volatile hydrocarbon components by oxidation [2]. The CS removes all particle precursors (volatile hydrocarbons and sulfur) and makes nucleation impossible downstream of the CS, whereas PMP system intends to suppress the nucleation by lowering the supersaturation ratio of the particle precursors. Ash particles and partially burned soot particles will make it past the CS, but re-nucleation will not occur with the CS.

Therefore, the CS is an ideal device to investigate the nature of particles under the PMP system. This study presents laboratory and vehicle experiments of diesel particle penetration/formation under PMP protocol using both PMP system and the catalytic stripper.

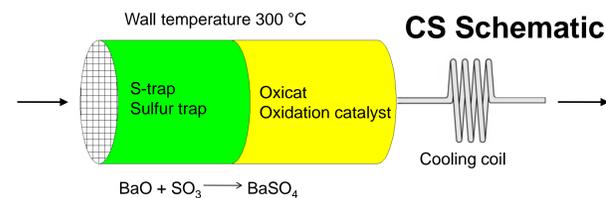
Objectives

- To evaluate the removal efficiency of the volatile species in the European PMP system using (a) challenging volatile aerosol in the laboratory; (b) exhaust sample from heavy-duty diesel vehicles operating over different cycles.
- To investigate the nature of nucleation mode particles downstream of the PMP system.
- To evaluate the PMP system with the Catalytic Stripper.

Schematics of PMP and CS

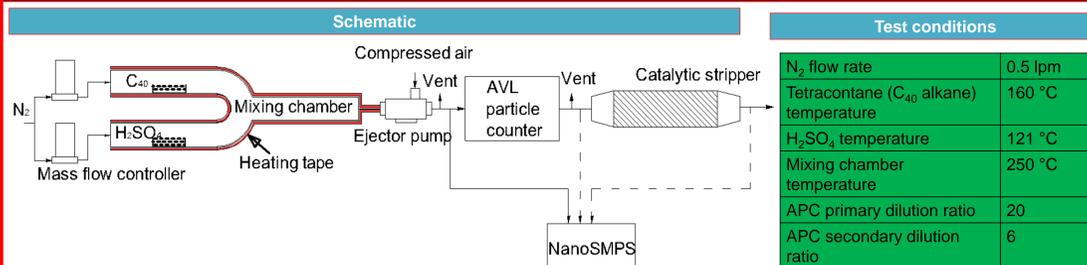


The PMP system used in this study was an AVL particle counter (APC) [3]. It consists of a primary chopper diluter heated to 150 °C, an evaporation tube heated to 350 °C, a perforated tube as the secondary diluter, and a TSI 3790 CPC with a cut point of 23 nm.

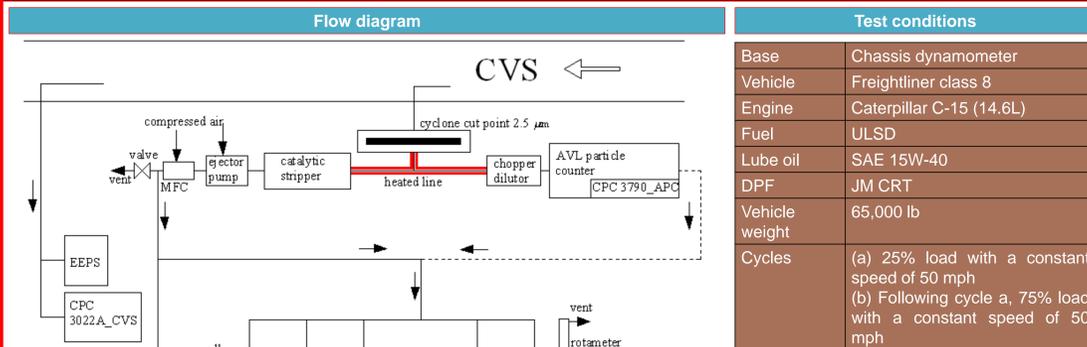


The Catalytic Stripper (CS) consists of two traps, S-trap and Oxicat. The S-trap removes SO₃ by reaction shown above and the Oxicat has an oxidation catalyst to help oxidize hydrocarbon compounds.

Tetracontane and sulfuric acid lab test



Chassis dynamometer test



CPC cut points (D₅₀) and sampling

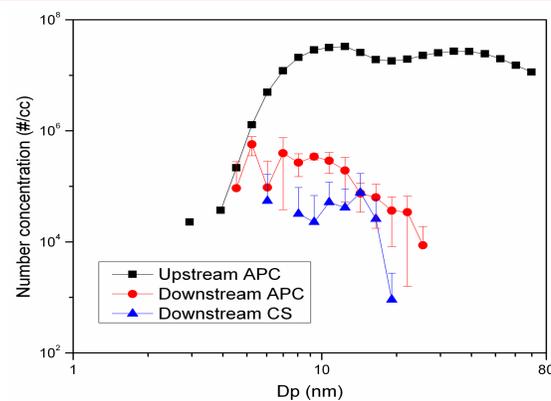
CPC model	D ₅₀ (nm)	location
3022A_CVS	7	Always at CVS
3025A	3	Alternate
3771	11	Alternate
3771_CS	11	Always at CS
3776	2.5	Alternate
3790_APC	23	Always at APC

Characteristics of tested cycles

- (a) 25% load: low exhaust temperature, storage of sulfate in the CRT, nucleation mode particle concentration low.
 (b) 75% load: high exhaust temperature, release of sulfate from the CRT, nucleation mode particle concentration high.

Results

Size distributions of tetracontane (C₄₀ alkane) and sulfuric acid (H₂SO₄) at upstream, downstream of AVL particle counter (APC), and downstream of the Catalytic Stripper (CS).



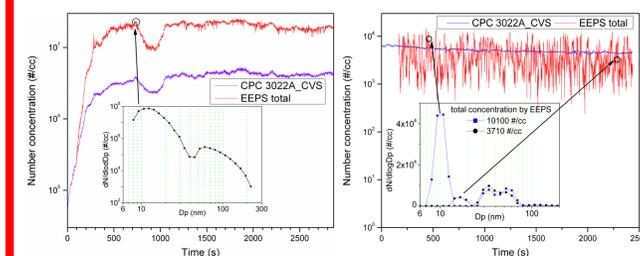
- At a dilution ratio of 120, the AVL particle counter (APC) was able to remove 99.9% of tetracontane (C₄₀ alkane) and H₂SO₄ particles. A small number of particles appeared to exist after the evaporation tube.
- The Catalytic Stripper (CS) was connected downstream of the APC to investigate whether these particles were volatile or solid. A large fraction of these particles were detected downstream of CS, suggesting these particles were solid.
- This result is consistent with previous study of a thermal denuder and a Catalytic Stripper [4]. The mechanism of solid particles formation downstream of the APC is not fully understood yet. More studies are needed.

Acknowledgements

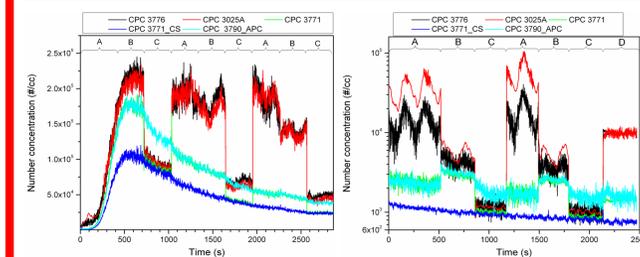
AVL for providing us the AVL particle counter and technical support.
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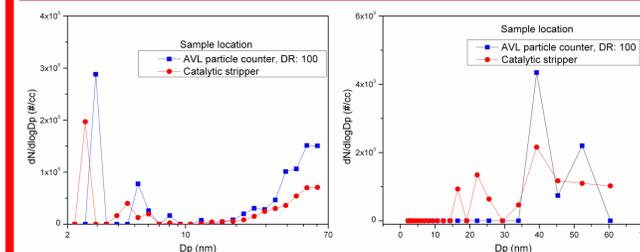
75% load 25% load
 Real-time number concentrations measured by CPC 3022A and EEPS in the CVS; insert of right figure shows two typical size distributions at different total concentrations (10100 #/cc and 3710 #/cc) measured by EEPS.



Real-time number concentrations measured by CPCs. Sampling location: A, AVL particle counter at dilution ratio of 500; B, AVL particle counter at dilution ratio of 100; C, Catalytic Stripper at a dilution ratio of 17; D, directly from CVS.



Size distribution measured by nanoSMPS downstream of AVL particle counter and catalytic stripper.



At 75% engine load, EEPS measured about one order of magnitude higher number concentrations than the 3022A, with particles primarily in the nucleation mode.

At lower engine load (25%), real-time particle number emission was much lower than that of higher load. Both EEPS and the 3022A agreed well, with less contribution from nucleation mode particles.

At both engine loads (75% and 25%), the lower cut point CPCs (3025A and 3776) always showed higher number concentrations than those of the higher cut point CPCs (3771 and 3790). The differences were more significant when sampling from the APC. However, at 25% engine load, the 3025A had a distinguishably higher concentration than the 3776 when sampling from the APC, with a dilution ratio of 500.

At both engine loads, concentrations downstream of the APC varied as a function of dilution ratio (DR). At 25% engine load, concentrations measured by both the 3025A and 3776 downstream of the APC with a DR of 500 were higher than those of CVS, while they were lower for DR of 100.

At both engine loads, the 3771 agreed well with the 3790_APC and the 3771_CS, while sampling downstream of the APC and the CS, respectively. However, number concentrations were always higher downstream of the APC than those downstream of the CS, indicating either the formation of particles in the APC or the better removal efficiency of volatiles by the CS.

At 75% engine load, size distributions measured by nanoSMPS showed particles below 10 nm were present downstream of both the APC and CS, which was consistent with the CPC data. The APC had higher concentration than the CS. However, at 25% engine load, no particles below 10 nm were seen from size distributions, which was inconsistent with the CPC data. This may be due to the low concentration at lower engine load and the diffusion loss in the nanoSMPS system.

Conclusions

- Lab tests with tetracontane (C₄₀ alkane) and H₂SO₄ showed that the APC was able to remove 99.9% volatile particles. However, appeared-to-be solid particles were formed downstream of APC. The mechanism of formation is not fully understood yet.
- Lower cut point CPCs measured higher concentrations than higher cut point CPCs downstream of both the APC and CS. The differences were more significant downstream of the APC.
- At 25% engine load, with a constant speed of 50 mph, the fact that the 3025A measured higher concentration than the 3776 downstream of APC needs further investigation.
- Number concentrations measured downstream of the APC varied as a function of APC dilution ratio. Comparing with CVS concentration, contradicting results were observed at 25% engine load.
- At both engine loads, number concentrations were always higher downstream of the APC than downstream of the CS, indicating either the formation of particles in the APC or the better removal efficiency of volatiles by the CS.
- Size distributions measured by nanoSMPS showed sub 10 nm appeared-to-be solid particles were present downstream of both the APC and CS at 75% load.

References

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