

Development of a Solid Exhaust Particle Number Measurement System Using a Catalytic Stripper Technology

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ABSTRACT

A solid particle number measurement system (SPNMS) was developed using a catalytic stripper (CS) technology instead of an evaporation tube (ET). The ET is used in commercially available systems, compliant with the Particle Measurement Program (PMP) protocol developed for European Union (EU) solid particle number regulations. The catalytic stripper consists of a small core of a diesel exhaust oxidation catalyst. The SPNMS/CS met all performance requirements under the PMP protocol. It showed a much better performance in removing large volatile tetracontane particles down to a size well below the PMP lower cut-size of 23 nm, compared to a SPNMS equipped with an ET instead of a CS. The SPNMS/CS also showed a similar performance to a commercially available system when used on a gasoline direct injection (GDI) engine exhaust.

While both the SPNMS/CS and the SPNMS/ET will likely perform similarly when used within the confinement of Euro 6/VI regulations, the SPNMS/CS has some advantages over an SPNMS/ET in its ability to evaporate and oxidize the volatile hydrocarbon materials instead of simply transferring them to the gas phase as done with the ET. Oxidizing the volatile hydrocarbon species promotes a faster droplet evaporation and reduces any potential artifact particle formation downstream of the CS, as compared with the ET, during dilution and/or cooling. This performance characteristic may give the SPNMS/CS a wider flexibility for measuring solid particle number from various combustion sources with high volatile particulate matter, well beyond the current scope of regulatory requirements. Relative to the potential sulfuric acid formation downstream of the CS, we were able to demonstrate in previous work that sulfuric acid

formation does not occur at the CS operating temperature of 300°C. In addition, using synthetic gas containing high concentration of SO₂ in air (~80 ppm), this CS showed high adsorption of SO₂ with no sign of SO₃ formation at its operating temperature of 300°C.

INTRODUCTION

Solid particle number (PN) emission has been introduced as a new regulatory metric for the first time in the history of particle emissions regulations from vehicles and engines. Euro 5/6 includes a solid PN standard for light-duty diesel vehicles at a level of 6×10^{11} part/km starting in 2009. By 2014, Euro 6 extends solid PN standard to include vehicles equipped with gasoline direct injection (GDI) engines, but the limit has not been set yet. By 2014, Euro VI for heavy-duty diesel engines also requires meeting a solid PN limit of 6×10^{11} part/kWh and 8×10^{11} part/kWh using the world harmonized transient cycle (WHTC) and world harmonized stationary cycle (WHSC), respectively. In the US, California Air Resources Board (CARB) LEV III proposal [1] includes optional solid PN standard for 2017, 2022 and 2025, but work is still underway to finalize the LEV III regulations. Currently, the solid particle number regulation focuses on solid particles measured with a condensation particle counter (CPC) having a 50% counting efficiency for electrical mobility particles 23 nm in diameter and > 90% counting efficiency for particles > 41 nm in diameter [2].

To measure solid PN from engines and vehicles, a Particle Measurement Program (PMP) [3] protocol has been developed under the United Nation (UN) Economic Commissions for Europe (ECE). The PMP protocol describes the system that can be used along with the calibration

requirements. Several publications have covered the PMP topics in more detail [4, 5, 6]. In addition, several PMP compliant commercially available instruments have been introduced and covered in different publications [7, 8, 9]. The PMP compliant system must sample PN from a full flow constant volume sampler (CVS) typically used in light-duty vehicle and heavy-duty engine certifications. A cyclone with a 50% cut size between 2.5 μm and 10 μm in aerodynamic diameter is used in the sample line from the full flow CVS to the PMP measurement system. The core of the PMP measurement system is shown in [Figure 1](#) [1]. It has two particle number dilution stages PND1 and PND2, with a heated evaporation tube (ET) in between the two dilution stages. The ET is maintained at a constant temperature between 300°C and 400°C. PND1 uses a heated dilution air between 150°C and 400°C and PND2 uses a cold dilution air below 35°C. PND1 can range from 10 to 200 and PND2 from 10 to 15 in dilution ratio.

The use of the ET in the PMP method has the potential of introducing volatile PN measurement artifact, most likely when sampling from engines with high volatile PN concentration. For example, recent work by Swanson and Kittelson [10] showed that with inlet concentration of 3.8 mg/ m^3 of tetracosane ($\text{C}_{24}\text{H}_{50}$) and sulfuric acid (H_2SO_4), a thermal denuder approach was not capable of removing all the volatile aerosol above 23 nm, compared to a catalytic stripper (CS) operating at the same temperature. This could be due to slow evaporation of volatile droplets inside the denuder or re-nucleation of volatile droplets during cooling by convection at the exit of the thermodenuder. Relative to volatile hydrocarbon treatment, there are two fundamental differences between an ET and a CS. The first difference is related to the fate of evaporated hydrocarbon species inside an ET and a CS. In the CS, the evaporated hydrocarbons diffuse to the wall of the catalyst and get oxidized into CO_2 and H_2O . The evaporation rate of a droplet entering the CS depends on the difference between the vapor pressure near the surface of the droplet and the partial pressure away from the droplet at the catalyst channel walls, which is effectively zero. For the ET, however, since the evaporated hydrocarbons are not consumed or oxidized, the evaporation rate can be slower than that in the CS because the evaporated materials are not removed and their partial pressure increases inside the ET leading to a slower evaporation rate. Later in this paper, we show an indication of this phenomenon between a CS and an ET using tetracontane particles. Ideally, in an ET, the evaporation of a droplet can stop completely when the partial pressure away from the evaporating droplet surface becomes equal to the vapor pressure near the droplet surface. The second difference between the CS and the ET approach is related to the gas composition at the outlet. Even if all volatile droplets are evaporated in an ET, there is still a potential for them to nucleate during cooling and/or dilution and cooling downstream of the ET. Hydrocarbon nucleation

downstream of a well designed CS does not exist due to the near 100 percent oxidation of hydrocarbon inside the CS.

The challenge hydrocarbon aerosol used in Swanson and Kittelson work had a much higher vapor pressure than the tetracontane ($\text{C}_{40}\text{H}_{82}$) typically used to challenge a PMP system. Using tetracontane may have shown higher artifact than the level reported, most likely due to lack of evaporation. Other work by Giechaskiel et al. [6] showed a similar artifact problem using a PMP system with a two-stroke engine, but most of the artifact aerosols were below 23 nm in diameter. Hands et al. [11] questioned in his work with two-stroke engine whether or not the PMP method was capable of removing efficiently the volatile aerosol and/or preventing nucleation during dilution and cooling. Thus, relative to the ET only, the current PMP method seems to have some shortcoming in two areas. First, it has the potential to nucleate and/or leave some artifact volatile aerosol in the sub-23 nm size range due to incomplete evaporation. It is unknown under what circumstances these aerosols cross the 23 nm size range and become counted. In addition, the cut-size of 23 nm is only part of an efficiency curve. Thus, even if the artifact aerosol is present at 15 nm for example, the PMP method will count them but at a lower efficiency than 50 percent. Second, because of the volatile artifact particle formation and/or lack of complete evaporation of volatile aerosols, the PMP method may not be suitable for any potential future regulation with a cut-size lower than 23 nm currently in place. So, while the ET use could be sufficient to deal with Euro 6/VI regulations, it has a potential to produce some measurement artifacts, particularly when its use is expanded to other applications with volatile PN or when using such system in research and development work for engine out measurements. As for the issue of producing measurement artifact with the CS due to the formation of SO_3 over the catalyst that results in sulfuric acid nucleation, we already showed in previous work using ammonium sulphate [12,13] that the CS operating temperature of 300 °C does not promote the formation of sulfuric acid droplet. In addition, we will show in this work that the CS does not promote the formation of SO_3 at the operating temperature of interest.

In 1995, Khalek and Kittelson [12] published on a CS for volatile particle removal. The CS consisted of a well characterized heated oxidation catalyst, along with a copper cooling coil tube. The purpose of the cooling coil was to cool the sample exiting the CS by convection down to ambient temperature level suitable for particle instruments. In 2007, Khalek [13] published on a similar CS work that was completed in 2002, but with a much lower particle loss. The low particle loss was mainly due to cooling by dilution, instead of using a cooling coil, to avoid thermophoretic losses. In the current work, we extended the same concept to develop a complete PMP measurement system using the CS instead of an ET. This paper describes a solid particle number

measurement system (SPNMS) that is based on a CS that can be easily interchanged with an ET. It discusses all calibration and performance checks of the system. It also highlights some of the issues that need further development and clarifications in the PMP protocol.

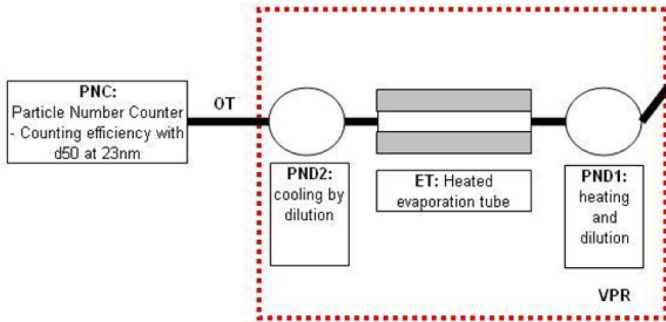


Figure 1. Core of PMP Measurement System for Solid Particle Number [1]

EXPERIMENTAL SETUP

SOLID PARTICLE NUMBER MEASUREMENT SYSTEM (SPNMS)

A flow diagram of the SPNMS is shown in Figure 2. It consists of a heated sample line, a 2.5 μm cyclonic separator, three stages of dilution, a CS, and a TSI Condensation Particle Counter (CPC) 3790. The first stage of dilution is an ejector diluter that is placed upstream of a micro diesel oxidation catalyst (m-DOC). Both the ejector pump and the m-DOC are placed in an oven environment that is maintained at 300°C. The first stage uses 300°C dilution air. It provides a dilution ratio in the range from 10 to 20. The second stage of dilution is a combination of an orifice and a dilution system that is located downstream of the m-DOC outside the oven. The second stage of dilution provides a dilution ratio between 10 and 20 using ambient dilution air at 25°C. The third stage of dilution provides a dilution ratio in the range from 1 to 3 to allow for total dilution ratios of up to 1200. The third stage of dilution uses ambient dilution air at 25°C.

The dilution air flow for each of the three stages of dilution is controlled and measured using a mass flow controller. The sample flow in the first and second stage of dilution is actively measured using a calibrated orifice with a delta P and inlet pressure and temperature. The total flow in the third stage of dilution is actively measured using the CPC 3790 orifice flow measurement. The m-DOC is similar to the one described in Reference 13. It was sized for this application using the same principles described in Reference 13, targeting high penetration of solid particles and high removal of volatile materials. Table 1 shows a description of the CS used in the PMP system. A similar volume ET can be substituted for the CS, described in Table 1.

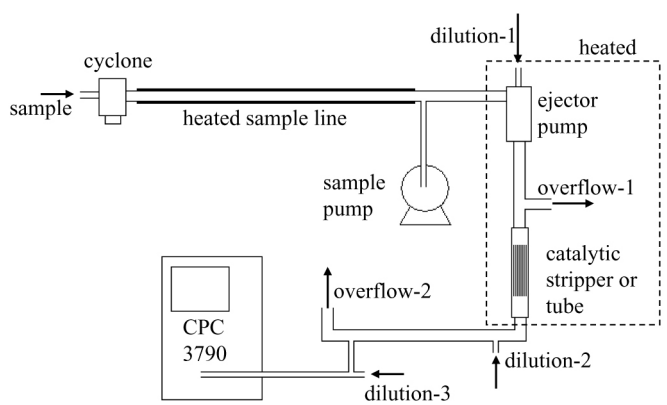


Figure 2. Flow Diagram of the SPNMS

Table 1. Oxidation Catalyst Specifications

Material	Ceramic Monolith
Wash Coat	Zeolite/Alumina
Catalyst	Platinum/Palladium
Geometry	Square Channels
Cell Density, # of cells per cm²	62
Nominal Catalyst Volume, cm³	5

A picture of the SPNMS in a test cell is shown Figure 3. It is controlled via an integrated datalogger and all data are recorded on a second-by-second basis. The system is configured to allow other instruments such as a CPC 3025A to measure in parallel with the CPC 3790.



Figure 3. The Solid Particle Number Measurement System (SPNMS)

PARTICLE GENERATION SYSTEMS

Sodium chloride (NaCl) particles were generated using a Collision atomizer, as shown in [Figure 4](#). Sodium chloride was dissolved in water and atomized in the Collision atomizer to produce droplet on the order of 5 μm . The outlet of the atomizer was heated and diluted using an ejector pump to enhance the evaporation of the droplet. After dilution, a silica gel diffusion dryer was used to help remove any water from the system. The dry aerosol exiting the diffusion dryer was neutralized using a Krypton 85 bipolar radioactive source before entering a differential mobility analyzer (DMA) for monodisperse size classifications. Efforts were made to generate a sodium chloride size distribution with a number mean diameter similar to the size of interest. This was done to avoid any large particles with more than one charge to interfere with the size classification with the DMA. For example, to produce a 30 nm monodisperse particle concentration at the outlet of the DMA, the polydisperse size distribution at the inlet of the DMA had a number mean diameter of about 30 nm. This was achieved by changing the salt concentration in the salt/water solution. An example of the NaCl size distributions is shown in [Figure 5](#).

Tetracontane particles were produced by inserting a small amount of tetracontane in a heated sample line with an air stream flow, as shown in [Figure 6](#). An example of the tetracontane size distributions is shown in [Figure 7](#).

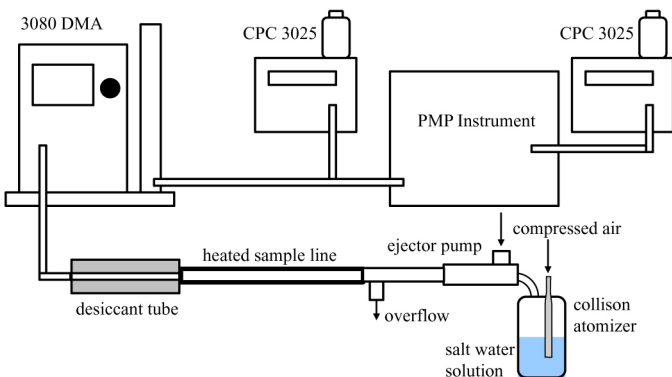


Figure 4. Sodium Chloride Particle Generation System

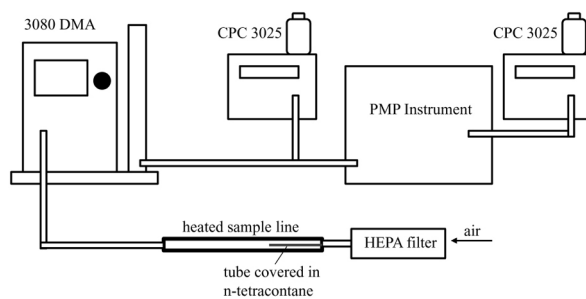


Figure 6. Tetracontane Particle Generation System

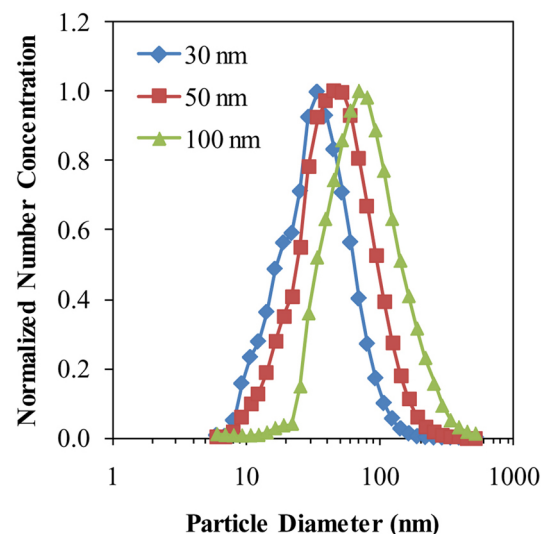


Figure 5. Example of NaCl Particle Size Distribution for 30, 50, and 100 nm Particle Penetration Experiments

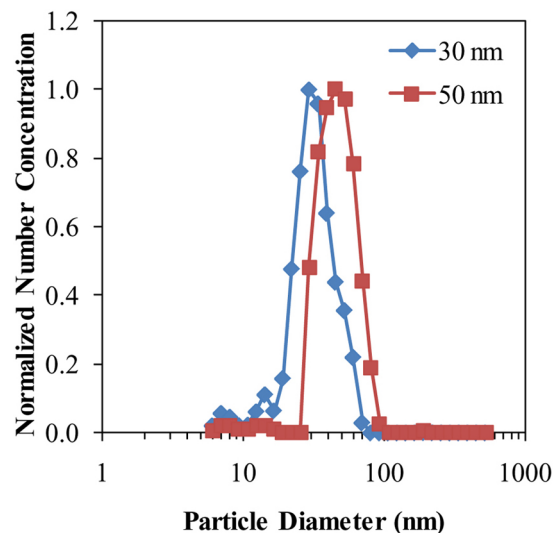


Figure 7. Example of Tetracontane Particle Size Distribution for 30 and 50 nm Particle Removal Experiments