

# A Miniature Catalytic Stripper for Particles Less Than 23 Nanometers

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## ABSTRACT

The European Emissions Stage 5b standard for diesel passenger cars regulates particulate matter to 0.0045 g/km and non-volatile part/km greater than 23 nm size to  $6.0 \times 10^{11}$  as determined by the PMP procedure that uses a heated evaporation tube to remove semi-volatile material. Measurement artifacts associated with the evaporation tube technique prevents reliable extension of the method to a lower size range. Catalytic stripper (CS) technology removes possible sources of these artifacts by effectively removing all hydrocarbons and sulfuric acid in the gas phase in order to avoid any chemical reactions or re-nucleation that may cause measurement complications. The performance of a miniature CS was evaluated and experimental results showed solid particle penetration was 50% at 10.5 nm. The sulfate storage capacity integrated into the CS enabled it to chemically remove sulfuric acid vapor rather than rely on dilution to prevent nucleation. Sulfuric acid re-nucleation was not observed until the challenge concentration was higher than 10 mg/m<sup>3</sup>. Additionally, the CS fully removed monodisperse tetracontane particles as large as 220 nm at a concentration of 10,000 part/cm<sup>3</sup>. A prototype "CS VPR" was constructed using the miniature CS and preliminary measurements from a field study are reported.

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## INTRODUCTION

Diesel exhaust contains a complex mixture of solid particles and semi-volatile material in the particle and vapor phases. Physical and chemical characterization of diesel exhaust aerosol enables a better understanding of potential health effects, effectiveness of alternative combustion technologies and emission control devices, and also the impact of new fuel and lubricant formulations on emissions. A primary source of solid particles is incomplete combustion in fuel rich zones, which leads to formation of fractal-like carbonaceous aggregates that are typically 30 - 300 nm in mobility diameter [1]. Smaller solid nanoparticles are also observed and it has been suggested that these may be single

carbon spheres [1, 2, 3, 4, 5, 6]. Additionally, the combustion of metal compound additives in lubrication oil or fuel additives leads to formation of solid metal oxide nanoparticles in the nucleation mode or decorated on solid aggregates [7, 8, 9, 10, 11]. Semi-volatile compounds are generally partially unburned hydrocarbons resulting from fuel and oil combustion. These compounds partition between the particle and vapor phases based on their volatility [12, 13, 14, 15, 16]. In addition, sulfur compounds in the fuel and oil are oxidized to sulfur dioxide during combustion and some of this can be further oxidized to sulfur trioxide in catalyzed emission control systems, which leads to the formation of sulfuric acid particles during exhaust dilution and cooling [17, 18, 19, 20]

Euro 5b regulations introduced a protocol for measuring the non-volatile particle number concentration for particles larger than 23 nm based on the findings of the Particle Measurement Program (PMP) methodology [21]. The EURO 5/6 standards established a solid particle number diesel emission standard of  $6.0 \times 10^{11}$  part/km (UNECE Regulation 83) that requires the use of this protocol for the removal of semi-volatile particles and material before the remaining (primarily carbonaceous) solid particles are measured. This standard effectively forced fitment of diesel particulate filters (DPFs) on all new European diesel cars from 2009. Targeting solid particles greater than 23 nm size is effective because DPFs efficiently remove smaller particles via diffusion making regulation at smaller sizes unnecessary. The PMP method specifies semi-volatile material is removed by a volatile particle remover (VPR) [22]. The VPR includes a hot dilution of at least 10 times with air heated to at least 150°C, a heated section with a wall temperature in the range 300-400°C, a room temperature dilution section to reduce the particle concentration to less than approximately 10,000 part/cm<sup>3</sup>, and a particle number counter (condensation particle counter) with 50% detection efficiency at 23 nm.

Evaluations of the VPR method have raised some concerns. Although the 23 nm solid detection limit helps to eliminate issues associated with partial evaporation, larger semi-volatile particles may not be completely evaporated to below 23 nm in all cases [23, 24]. Furthermore, as shown theoretically by Giechaskiel and Drossinos [25] and experimentally by Giechaskiel et al. [26], the VPR approach has concentration limits. Re-nucleation occurs after passage through the VPR when the concentration of hydrocarbons is greater than 25 mg/m<sup>3</sup> or when the concentration of hydrocarbons is greater than 5 mg/m<sup>3</sup> in the presence of sulfuric acid aerosol. An additional concern of the method, considering that it will be extended to gasoline and heavy duty engine regulations, is that large numbers of solid particles smaller than 23 nm can exist in heavy duty diesel and gas engine exhaust that are not counted [27].

There are alternatives to the standard heated evaporation tube approach used in commercial VPR systems such as the catalytic stripper (CS) [23, 28, 29] or thermal denuder (TD) [30]. These alternative techniques may be used to better understand possible artifacts with the current method and possibly be used to extend the method to the measurement of solid particles smaller than 23 nm. However, experiments by Johnson et al. [31], Giechaskiel et al. [26], Swanson et al. [32], and Zheng et al. [33] confirm that application of the PMP method to count truly solid particles smaller than 23 nm is challenging. It is possible that use of CS technology may reduce artifact formation when used in conjunction with the PMP methodology but there are a number of remaining issues that motivate additional study. For example, there is no standard for sulfuric acid particle generation and removal. It is critically important to consider the role of sulfuric acid when evaluating the performance of solid particle counting

instruments below 23 nm. Previous studies have shown standard atomization techniques result in residual particle artifacts due to contaminants [23] and that solid artifacts may be associated with evaporation of laboratory generated sulfuric acid aerosols, but it is unclear if they are related to the generation technique [32]. The presence of contaminants that manifest as residual particles limits the ability to estimate the capacity of a thermal treatment device like the CS to fully remove semi-volatile particles because contaminants may mask their incomplete removal. Another issue is the fact that standard procedures require removal efficiencies to be reported on a simple percentage basis to demonstrate compliance with the current standard [25, 29]. This efficiency statistic does not provide the information required to understand if particles measured downstream result from re-nucleation, incomplete evaporation, background contamination, a leak, or an artifact related to particle generation. To fully evaluate these technologies, measurements of both the downstream particle size distribution and volatility characteristics are required to elucidate whether residual particles are solid artifact or semi-volatile material.

Here we report on the design and evaluation of a miniature CS operated at 1.5 L/min that was optimized for performance in the particle size range 3 to 23 nm. Results are discussed in the context of diesel emissions and the PMP methodology because these methods provide a standard approach for characterizing and validating thermal particle treatment devices. However, CS technology and the characterization results are not limited to the PMP application. Other applications for the CS include measurements of ambient air quality and particles from various combustion processes including domestic heating and gas turbine exhaust. These applications may have greater or lesser requirements, so this study aimed to establish performance limits for removing volatile sulfuric acid and hydrocarbon particles. Results are reported as removal efficiencies based on mass and number because “mass” removal is indicative of the amount of material that is removed by diffusion which can be related to theoretical performance calculations, while the removal of particles based on number enables comparison with current standards. One specific application of the miniature CS is to replace the heated evaporation tube in a commercially available VPR [34]. In this regard, results from measurements with a prototype CS VPR are also presented.

## Aerosol Instrumentation

Particle size and concentration were measured upstream and downstream of the CS using two scanning mobility particle sizers (SMPS). The upstream SMPS had a TSI Long Differential Mobility Analyzer (DMA) and a TSI 3025A condensation particle counter (CPC). The SMPS was operated with sheath and sample flows of 15 and 1.5 L/min, respectively, giving a measurement size range of about 7 to 300 nm. A nano-SMPS consisting of TSI nano-DMA and a

TSI 3776 CPC was used for the downstream measurements. It was configured to size particles from 3 to 60 nm. Upstream and downstream concentrations and size distributions were usually measured simultaneously. Results from each SMPS were corrected for column diffusion losses. Transport losses to each instrument were minimized by using short lines and electrically conductive tubing. In all cases, reported size distributions include error bars that were calculated as the standard deviation from typically five measurements made at each test condition. Total mass concentrations were calculated by integrating the SMPS size distributions, converting them to a total volume basis, and then multiplying this by the density of the particles (1.6 g/cm<sup>3</sup> for sulfuric acid and 0.82 g/cm<sup>3</sup> for tetracontane) at the measured relative humidity. For the cases where the entire distribution was not measured, the mass concentration was based on a lognormal fit to the experimental data.

## Miniature CS Specifications and Calculated Performance

A CS is a catalytic device that removes semi-volatile hydrocarbon particles through evaporation and oxidation. Design of a CS requires consideration of the impact of substrate geometry and temperature on particle evaporation rates, particle loss, and the diffusion of gas molecules in the channels [23, 28].

### CS geometry

The miniature CS is a cylindrical, monolithic device with parallel flow-through channels along its axis. The ceramic substrate used was coated with a high surface area proprietary washcoat that contained highly dispersed platinum group metal (PGM) crystallites enabling rapid oxidation of hydrocarbons. Alkaline components are incorporated into part of the CS to aid in the storage of sulfur compounds. The catalytically active monolith was retained in a stainless steel mantle with an intumescent mat. The mantle had welded stainless steel cones for attachment to inlet and exit streams. The mantle was resistively heated with the temperature set-point of 300°C based on measurement of the temperature along the central axis of the CS midway between the inlet and outlet. For laboratory experiments, a finned tubular heat exchanger was located downstream of the CS to cool the gas to ambient temperature. Table 1 provides the geometry of the miniature CS, which was determined based on the analysis presented in the following sections.

**Table 1. Miniature CS specifications and calculated performance. Diffusion coefficients used to calculate tetracontane and sulfur trioxide penetration were  $7.89 \times 10^{-6}$  and  $2.1 \times 10^{-5}$  m<sup>2</sup>/s, respectively [35].**

|                                             |       |                       |
|---------------------------------------------|-------|-----------------------|
| Core length                                 | 3.8   | cm                    |
| Core diameter                               | 1.15  | cm                    |
| Cell density                                | 600   | cells/in <sup>2</sup> |
| Wall thickness                              | 2.5   | mil                   |
| Operating temperature                       | 300   | °C                    |
| Inlet flowrate                              | 1.5   | L/min                 |
| C <sub>40</sub> H <sub>82</sub> penetration | 0.002 | -                     |
| SO <sub>3</sub> penetration                 | 5E-8  | -                     |
| d <sub>50</sub> size                        | 7     | nm                    |

### Effect of flowrate on particle penetration, evaporation, and vapor removal

The CS geometry is fixed though the choice of cell density and physical dimensions. For a fixed geometry, the operating temperature and flowrate dictate performance, although performance needs may vary depending on application. In general, the design parameters for the CS reflect a balance between solid particle loss, flowrate, residence time, operating temperature, and vapor removal. Guidance for performing these calculations can be found in Khalek [23], Stenitzer [35], and Abdul-Khalek and Kittelson [28]. Basic design considerations are summarized in the following.

To measure solid particles smaller than 23 nm, the loss of small solid particles in the CS channels must be minimized. At this size the primary loss mechanisms are diffusion and thermophoresis. Diffusion effects increase with decreasing particle size but thermophoresis acts independently of particle size in the free-molecular regime [36]. The calculated solid particle penetration in the miniature CS including thermophoretic loss in the heat exchanger is 50% at 7 nm. The size in which 50% of particles penetrate is referred to as the d<sub>50</sub> size. In addition, semi-volatile particles must fully evaporate in the CS and their vapors must be removed. The evaporation time of a 100 nm tetracontane particle was estimated using a free-molecular regime expression for the rate of particle diameter change (dD<sub>p</sub>/dt) due to evaporation as shown in Equations (1) and (2),

$$\frac{d(D_p)}{dt} = \frac{2 \cdot M \cdot (P_\infty - P_d)}{\rho_p \cdot N_A \cdot \sqrt{2 \cdot \pi \cdot m \cdot k_B \cdot T}}, \quad (1)$$

$$P_d = P_s \cdot \exp\left(\frac{4 \cdot \gamma \cdot M}{\rho_p \cdot R \cdot T \cdot D_p}\right), \quad (2)$$

where  $M$  = molecular mass (0.563 kg/mol),  $P_\infty$  = ambient vapor partial pressure ( $0.5P_s$ ),  $P_d$  = saturation pressure at the droplet surface (Kelvin effect),  $\rho_p$  = particle density (820