

Use of a Catalytic Stripper as an Alternative to the Original PMP Measurement Protocol

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ABSTRACT

The Particle Measurement Programme (PMP) developed an exhaust particle number measurement protocol that has been adopted by current light duty vehicle emission regulations in Europe. This includes thermal treatment of the exhaust aerosol to isolate solid particles only and a number counting device with a lower cutpoint of 23 nm to avoid measurement of smaller particles that may affect the repeatability of the measurement. In this paper, we examine a potential alternative to the PMP system, where the thermal treatment is replaced by a catalytic stripper (CS). This offers oxidation and not just evaporation of the volatile components. Alternative sampling systems, either fulfilling the PMP recommendations or utilizing a CS, have been explored in terms of their volatile particle removal efficiency. Tests have been conducted on diesel exhaust, diesel equipped with DPF and gasoline direct injection emissions. The results showed that the CS offers similar performance characteristics to the PMP when tested on diesel exhaust. In tests with the gasoline vehicle, the CS has been shown of leading to lower particle concentrations than the PMP, indicating that a larger number of particles can be removed as volatiles. Moreover, steady speed tests at 120 kph revealed that the PMP protocol was not sufficient in removing particles below 10 nm, which were completely eliminated when the CS was positioned downstream of an evaporation tube. The results of the study once more confirm the robustness of the PMP protocol for diesel exhaust sampling but also suggest that more analysis is needed before extending the protocol to other vehicle types and/or particle sizes.

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INTRODUCTION

The Particle Measurement Programme (PMP) protocol has been successfully taken up by European emission control regulations [1] to limit the number of 'solid' particles emitted by light duty vehicles. Based on this, Euro 5 and Euro 6 diesel passenger cars and light commercial vehicles in Europe are only granted a type-approval if they emit below 6×10^{11} km⁻¹ particles over the certification test. In 2012 [2], number-based emission limits were also introduced for direct-injection spark-ignition cars and light commercial vehicles. Two phases are foreseen, one with a relaxed limit at 6×10^{12} km⁻¹ to be introduced in 2014 and then a second phase in 2017 with a limit value equal to the one for diesel vehicles.

The definition of 'solid' particles in the European regulations is an operational one. By 'operational', one means

a definition which is based on the conventions and limitations imposed by the sampling protocol adopted for the measurement of such particles. This is in analogy to the definition of particulate matter (PM) by automotive regulations, which is also an operational one. PM has for years been defined as the material collected on a filter within a given temperature range following exhaust dilution. Both the filter material and the temperature range of sampling may differ around the globe hence alternative definitions of PM may hold in different regions. For example, US EPA [3] requires the filter temperature to be maintained within 47±5°C while European regulations only limit this to below 52°C [4]. Therefore PM is differently defined in the two regions. Similarly, 'solid' particles in the European regulations are particles that are detected by a particle number counter having a 50% counting efficiency at 23 nm following hot dilution (minimum 10:1) at a temperature

>150°C and an evaporation tube at 300-400°C [4]. Alternative definitions for 'solid' particles will also have to make similar references to sampling practices.

Due to this operational nature of the definition, solid particles measured by the PMP protocol have received significant criticism. Most importantly, this definition is considered to leave a significant fraction of the exhaust aerosol potentially uncontrolled, i.e. these non-volatile particles that fall below 23 nm. Also, there is concern that the protocol may still leave volatile particles to survive sampling and erroneously be counted as solids (e.g. [5]). The whole criticism and the response to this is summarized in a thorough review article on PMP developments by Giechaskiel et al. [6] and need not be repeated here. In a nutshell though, PMP was primarily developed as a way to enforce the application of Diesel Particle Filters (DPFs) in all diesel vehicles and compromises had to be made to enable measurement repeatability and technical and economical feasibility of the whole system. PMP has been successful in this respect as particle filters have become mandatory for all diesel passenger cars at Euro 5 and Euro 6, heavy duty trucks at Euro VI and even raises possibilities for gasoline particle filters introduction in the long run [7].

PMP has also been the motivation for mobilizing research on alternative particle number sampling systems, which may potentially overcome some of its limitations. The catalytic stripper (CS), originally proposed by Khalek and Kittelson [8], has been the most popular candidate for such a system. In the CS, organic species with the potential to nucleate are oxidized, thus the possibility for renucleation downstream of the sampling system is eliminated. This first prototype consisted of a commercial oxidation catalyst heated at 300°C along with a cooling coil tube to reduce the temperature at ambient levels. Later, a similar catalytic stripper was combined with a downstream vortex tube diluter to minimize thermophoretic losses [9]. In a more recent study [10], a downsized catalytic stripper replaced the evaporation tube in a PMP compliant system.

In such a catalyzed system, oxidation of sulfur to form sulfates that may lead to sampling artifacts has always been of some concern. To address this issue, a modified version of the catalytic stripper using a sulfur trap upstream of the catalyst was tested by Stenitzer [11]. This system was used for determining the non-volatile part of vehicle emissions [12,13,14] and was found superior to a thermodenuder [15].

An alternative to this CS concept [15, 16] consisted of an oxidation catalyst, this time followed by the sulfur trap. This is considered appropriate for sampling exhaust aerosol from vehicles powered by current low-sulfur fuels. In such a case, the sulfur trap may offer sufficient capacity to store sulfates throughout the lifetime of the stripper. Amanatidis et al. [17] characterized this version of the stripper in terms of its PMP-compliant characteristics (particle penetration, hydrocarbon aerosol removal) and in terms of its sulfur capacity and hydrocarbon breakthrough performance. In the current study, we explore the performance of this new CS version as an

alternative to PMP by sampling exhaust aerosol from a variety of passenger cars, including diesel, diesel equipped with DPF, and gasoline direct injection, over transient and steady state conditions.

EXPERIMENTAL

Catalytic Stripper

The CS evaluated in this study consisted of a cordierite monolith (L: 39 mm, D: 17 mm) with silica-alumina coating, a cell density of 400 cells per square inch, and 2.5 mil wall thickness. The Pt-based oxidation catalyst was 26 mm long with the remaining part consisting of the barium oxide adsorber (sulfur trap). Most of the tests were conducted at a flowrate of 1.5 l/min, with minor departures from this in some tests trying to accommodate alternative particle number counting devices downstream of the CS. The sample residence time (RT) in the CS was approximately 0.35 s at this flowrate and at operation temperature (300°C). Particle losses at this temperature range from 39%, 27%, 26%, and 25% at 15, 30, 50, and 100 nm, respectively.

Vehicle Testing

The vehicles used in this study were a Euro 4 diesel and a stoichiometric Euro 5 direct injection spark ignition (DISI) one (Table 1). The diesel vehicle in its original configuration was equipped with an oxidation pre-catalyst and a two-stage oxidation underfloor catalyst. In this study the diesel vehicle was tested in alternative configurations in order to simulate various exhaust emission levels (Table 2). On one configuration the vehicle was tested with the underfloor catalyst completely removed. In two other configurations, two different DPFs were used in place of the underfloor catalyst. DPF #1 was a regular non-catalytic SiC one (5.66×6 in², 300 cpsi, 2.5 l, 12 mm substrate thickness). DPF #2 was similar to DPF#1 but was artificially compromised by removing some 40% of its inlet channel plugs. Our intention with this filter was to simulate a damaged DPF and also to study the sampling system behavior at such intermediate emission levels.

Both vehicles were tested with commercially available fuel complying with Regulation 2009/30/EC. For diesel this means a maximum sulfur content of 10 ppm wt and a maximum biodiesel content of 7% vol. For gasoline, this also means max sulfur content of 10 ppm wt and 3.7 % wt oxygen content.

Table 1. Test vehicle specifications.

	Honda Accord i-CTDi	VW Golf TSI
Fuel	Diesel	Gasoline
Displacement [cm ³]	2204	1390
Fuel Injection System	Common Rail	Direct Injection Spark Ignition
Max Power [kW/rpm]	103/4000	90/5000
Max Torque [Nm/rpm]	340/2000	200/1500
Aspiration	Turbocharged	Turbocharged Stoichiometric
Cylinders	4	4
Certification	Euro 4	Euro 5
Year	2006	2012
Mileage [km]	~80 000	350

Table 2. Vehicle exhaust gas aftertreatment configurations.

Vehicle	Configuration	Exhaust gas aftertreatment
Honda Accord i-CTDi	Without DPF	EGR, Pre-oxidation catalyst
	Compromised DPF	EGR, Pre-oxidation catalyst, partially damaged DPF
	Regular DPF	EGR, Pre-oxidation catalyst, DPF
VW Golf TSI	Default	3-Way Catalyst

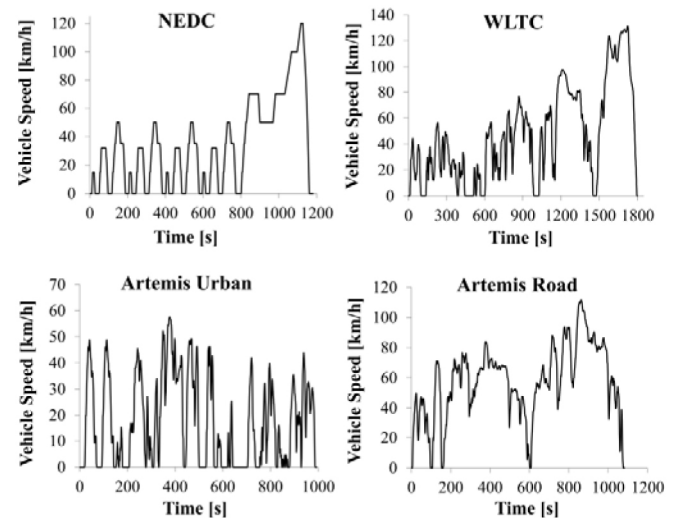
Measurement Protocol

The measurement protocol consisted of both transient and steady speed tests. Both vehicles were tested over the New European Driving Cycle (NEDC) which is the legislated cycle for the type approval procedure of light duty vehicles in Europe. This driving cycle was conducted for both “cold” and “hot” engine start conditions. Additionally, three alternative driving cycles were included in the test procedure; the so-called Artemis Urban and Road driving cycles, which are considered to be more representative of the real-world urban and rural driving conditions, and the Worldwide harmonized Light-duty Test Cycle (WLTC) which is currently under development (version 5) as a replacement to the NEDC for the certification of Euro 6 light duty vehicles. Due to measurement constraints, WLTC was executed as a hot-start cycle. The speed profile vs. time of each cycle is presented in Figure 1.

In addition, tests at constant cruising speeds of 50 kph and 120 kph were conducted in order to study the performance of the sampling systems at steady-state conditions.

Airborne Particle Sampling Systems

All vehicles were tested at the light duty chassis dynamometer of the Lab of Applied Thermodynamics. The exhaust gas was primarily diluted and conditioned following Constant Volume Sampling (CVS). A 6 m long corrugated stainless steel tube transferred the exhaust from the vehicle tailpipe to the CVS tunnel inlet. A flowrate of 600 m³/h (calculated at normal conditions) was maintained in the CVS tunnel by a positive displacement pump. The dilution air was filtered by a HEPA class H13/EN1822 filter at the inlet of the dilution tunnel and the background solid ≥ 23 nm particle concentration in the tunnel was monitored in regular intervals and remained in the order of 10 cm⁻³.

**Figure 1. Vehicle speed profile vs. time of the driving cycles used in the test protocol.**

A number of different sampling configurations were then evaluated in terms of their particle removal performance, with the different vehicle configurations. These sampling systems are schematically shown in Figure 2 and are described in the following list:

1. **No thermal pre-treatment:** The dilution system consisted of two cascaded Dekati ejector diluters. All devices were operating at ambient temperature.

2. **PMP:** An ejector diluter operating at 150°C in series with an evaporation tube at 350°C wall temperature (RT=0.25 s), followed by a second ejector diluter at ambient temperature. This has been shown to be a favorable PMP configuration resulting in high volatile particle removal efficiency and very low particle losses [18]. An in-house intermediate dilution stage was used downstream of the evaporation tube only during the diesel vehicle tests without DPF to increase the total dilution ratio (DR 35:1).