THE PMP-COMPLIANT CATALYTIC STRIPPER

APPLICATION NOTE CI-0010

Background

A limit on particle number (PN) has been part of the European vehicle emission legislation since the enactment of stage EURO 5b in 2011. Specifically, the UNECE R49/R83 regulation defines the measurement set up as part of the Particle Measurement Programme. The Catalytic Stripper (hereon CS) is a vital component of the highly efficient Volatile Particle Remover (VPR) system (shown in the diagram below).
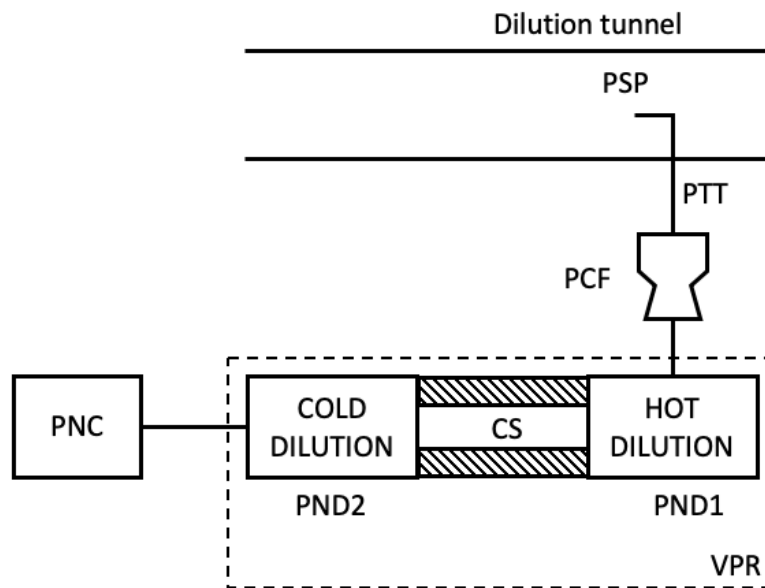

Figure 1: Schematic of the dilution tunnel measurement system in the PMP protocol

Acronym	Definition	Acronym	Definition
PSP	Particle Sampling Probe	VPR	Volatile Particle Remover
PTT	Particle Transfer Tube	PNC	Particle Number Counter
PCF	Particle pre-classifier	CS	Catalytic Stripper
PND	Particle Number Diluter	PND2	Particle Number Diluter 2

Catalytic Instruments GmbH & Co.KG • Zellerhornstrasse 7 • D-83026 Rosenheim
Tel: +49 8031 901 777-0 • **Fax:** +49 8031 901 777-5 • **email:** info@catalytic-instruments.com
www.catalytic-instruments.com

Typically, the CS is placed between a two-stage (hot and cold) dilution system, to remove any non-solid particles and gas-phase hydrocarbons. The first dilution stage operates between 150 – 400°C ±10°C, and dilutes by a factor of at least 10. The sample then enters the CS (which must be kept in the temperature range 300ºC – 400ºC ±10ºC; Type Approval document 2017/654), whereby semi volatile organic compounds (SVOCs) in the aerosol and gaseous phase are converted into CO_2 and H_2O. Solid particles (e.g. fractal aggregates such as soot) remain unchanged and pass through the CS into the optional second dilution stage, typically operated at ≤ 35ºC, then the sample passes through to the Particulate Number Counter (PNC).

CS015 particle losses have been **fully characterised** and are presented in Application Note 0009. In summary, the CS015 takes contains a cooling section to bring the aerosol sample down to room temperature, so as to not damage other lab equipment downstream. This induces thermophoretic loss, in the cooling section, and the total particle losses are < 40% at 100 nm. However, as stated above, the CS015 is not the CS referred to in the PMP legislation. Only the diffusion losses shown in the graphs are applicable for the "VPR-CS" alone, as the thermophoretic loss is dependent on the **entire VPR configuration**. The diffusion loss at 100 nm is around 1-2%.

Particle Concentration Reduction Factor (PCRF)

You may well be familiar with PCRF, or the particle concentration reduction factor, $f_r(d_i)$. The aim of the PCRF is to ensure that sampling designs permit sufficient concentrations of smaller aerosol particles through to the particle number counters (PNCs). An infinitely long pipe will lose aerosol particles smaller than 100 nm to the walls of the tube, even with laminar flow, due to diffusion. The diffusion in the CS is slightly higher than that of a pure Evaporation Tube (ET), due to the increase surface area. However, unlike the ET, there will be no artefacts of renucleated particles tricking PNCs into thinking solid particle emissions have increased!

The current PMP legislation states that the VPR system (as a whole) must have no more than a 30% and 20% particle concentration reduction factor (PCRF) compared

Catalytic Instruments GmbH & Co.KG • Zellerhornstrasse 7 • D-83026 Rosenheim
Tel: +49 8031 901 777-0 • **Fax:** +49 8031 901 777-5 • **email:** info@catalytic-instruments.com
www.catalytic-instruments.com

to 100nm for particles of 30nm and 50nm, respectively (section 2.2.2.1), and is calculated as written in 2.2.2.2.:

> The particle concentration reduction factor at each particle size $f_r(d_i)$ shall be calculated using the following equation:
>
> $$f_r(d_i) = \frac{N_{in}(d_i)}{N_{out}(d_i)}$$
>
> where:
>
> $N_{in}(d_i)$ is the upstream particle number concentration for particles of diameter d_i;
>
> $N_{out}(d_i)$ is the downstream particle number concentration for particles of diameter d_i;
>
> d_i is the particle electrical mobility diameter (30, 50 or 100 nm).
>
> $N_{in}(d_i)$ and $N_{out}(d_i)$ shall be corrected to the same conditions.

The off-the-shelf CS015 is <u>not</u> a PMP-device but can be used as part of a PMP setup, namely, within the VPR system. However, we routinely optimise our devices for use in PMP measurement, and if you require a PMP-compliant CS please contact us directly for a solution to your needs.
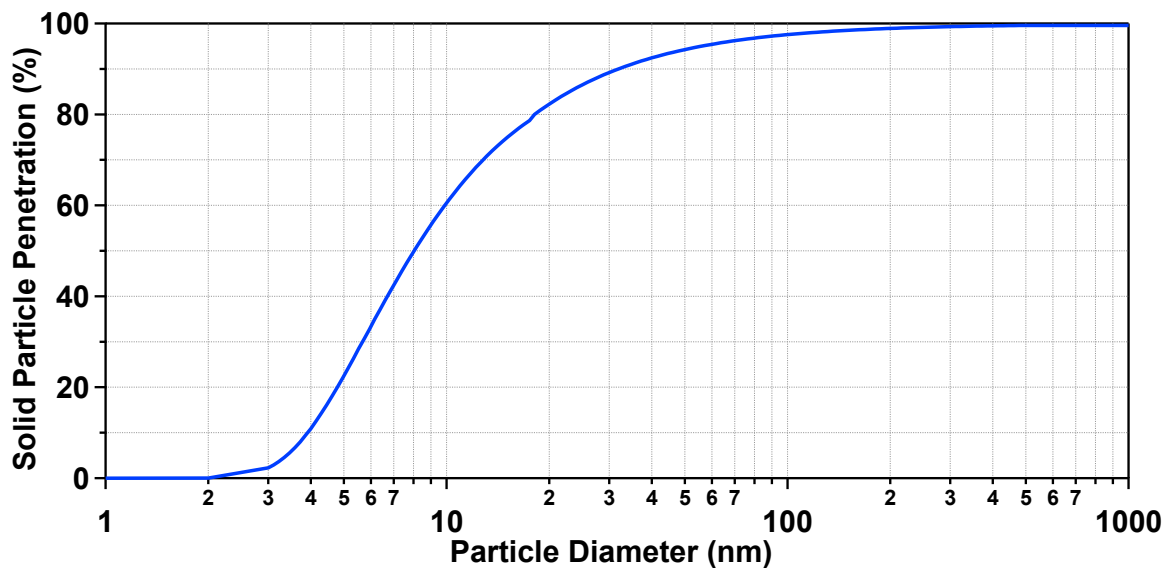

Figure 2: Solid particle penetration as a function of solid particle diameter (i.e. electrical mobility diameter from a DMA).

As we make the change to the CS, it's good to document the losses within the "CS" section of a VPR system (e.g. Fig. 2, above). The table below shows "the PCRF of the VPR-CS only", with the legislative limits;

Catalytic Instruments GmbH & Co.KG • Zellerhornstrasse 7 • D-83026 Rosenheim
Tel: +49 8031 901 777-0 • Fax: +49 8031 901 777-5 • email: info@catalytic-instruments.com
www.catalytic-instruments.com

	15 nm*	30 nm	50 nm	100 nm
VPR-CS	35%	10%	4%	1-2%
PCRF limit	100%*	30%	20%	N/A

Table 1. PCRF limits for VPR systems
proposed update to PMP legislation for sub 23 nm (SPN10) measurement

This means that the first (hot) and second (cold) dilution stages have plenty of headroom for further losses, and that the inclusion of a CS will not make the VPR fail PCRF. For reference, the bulk of thermophoretic losses in a VPR occur following the CS or ET into the secondary particle dilution system (PND2), but this is easily optimised.

A Futureproof Solution

Striving to improve tailpipe emission regulation further still, significant time and research has been spent in pushing the sampling to ever smaller particle sizes. To this effort, the proposal is to set the PCRF limit at 100% for 15nm particles (source: UNECE PMP). For reference, our CS has around 70% penetration (i.e. 30% solid particle loss) at 15nm, and thus is not just completely compliant with the new proposal, but gives a lot of headroom for the rest of the VPR system to comply.

Further, our CS is increasingly advised instead of the previous Evaporation Tube (ET) only approach due to potential re-condensation of volatiles specifically in the sub-23nm range (e.g. PEMS4Nano/Horiba, Ricardo AEA). At present, the CS is optional for current 23 nm PMP measurement, and is expected to be the only solution for sub 23 nm (SPN10) in upcoming legislation.

Volatile Particle Removal

Current legislation dictates that a VPR must achieve a > 99.0 % vaporization of 30 nm tetracontane ($CH_3(CH_2)_{38}CH_3$) particles, with an inlet concentration of ≥ 10,000 per cm³, by means of heating and reduction of partial pressures of the tetracontane. This is effectively removed by a VPR including just an ET let alone a CS. However, future PMP legislation is very likely to include the following additional challenge of:

Catalytic Instruments GmbH & Co.KG • Zellerhornstrasse 7 • D-83026 Rosenheim
Tel: +49 8031 901 777-0 • Fax: +49 8031 901 777-5 • email: info@catalytic-instruments.com
www.catalytic-instruments.com

> 99% removal efficiency of polydisperse alkane (e.g. Eicosane, decane or higher) or emery oil with count median diameter > 50 nm and mass > 1 mg/m^3

Application notes 0007 and 0007_2 present data on the removal efficiency of the CS with high concentrations of emery oil to test its removal efficiency. In short, the CS volatilises and converts these aerosols into gaseous products, without risk of re-nucleation artefacts downstream. In fact, the CS works so well that even at concentrations *without* primary dilution, these semi-volatile aerosol particles are completely removed.

Summary

The Catalytic Stripper is PMP compliant as part of a VPR system, and its use ensures no re-nucleation artefacts. Operated accurately at 350ºC, the CS has been designed from the ground up to sit in the middle of the recommended operational temperature range for the ET section, and allows significant headroom for PCRF losses, including the proposed improvements to PMP down to 10 nm. The newly proposed, harder-to-remove challenge aerosol is converted to non-re-nucleating gases as efficiently as possible, whilst simultaneously permitting the high penetration of solid aerosol particles.

Please contact us if you have any further questions for your PMP-compliant measurement needs: info@catalytic-instruments.com

Further Reading

UNECE PMP Regulation and Working Group Sessions:

https://wiki.unece.org/pages/viewpage.action?pageId=2523173

Catalytic Instruments GmbH & Co.KG • Zellerhornstrasse 7 • D-83026 Rosenheim
Tel: +49 8031 901 777-0 • **Fax:** +49 8031 901 777-5 • **email:** info@catalytic-instruments.com
www.catalytic-instruments.com

References

Abdul-Khalek, I.S.; Kittelson, D.B. (1995). Real time measurement of volatile and solid exhaust particles using a catalytic stripper. Society of Automotive Engineers, 950236.

Amanatidis, S.; Ntziachristos, L.; Giechaskiel, B.; Katsaounis, D.; et al. (2013). Evaluation of an oxidation catalyst ("catalytic stripper") in eliminating volatile material from combustion aerosol. J. Aerosol Science, 57, 144-155

Giechaskiel, Barouch, et al. "Sampling of Non-Volatile Vehicle Exhaust Particles: A Simplified Guide." SAE International Journal of Engines, vol. 5, no. 2, 2012, pp. 379–399. JSTOR, www.jstor.org/stable/26278367. Accessed 9 Jan. 2020.

Gormley, P.G., Kennedy, M., 1949. Diffusion from a stream following through a cylinderical tube. Proceedings of Royal Irish Academy 52, 163–169

Housiadas, C., and Drossinos, Y., 'Thermophoretic Deposition in Tube Flow', Aerosol Sci. Techn., 39:304-318, 2005.

Swanson, J.; Kittelson, D. (2010). Evaluation of Thermal Denuder and Catalytic Stripper Methods for Solid Particle Measurements. J. Aerosol Science, 41:12, 1113 – 1122