10^{th} Anniversary

of the PMP Golden Instrument

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In summer 2002, PMP ran an extensive experiment with about 15 different particle measuring principles at a heavy duty engine with DPF on the test bench at EMPA in Switzerland. The main conclusion from this impressive campaign was the far-reaching recommendation for the best metric: It was the Number Concentration of Solid Particles - "PN" - that was to form the future particle standard for vehicle type approval in Europe.
Now the metric was set and so was the corresponding measuring instrument, the Condensation Particle Counter. However, the method for separating solid from volatile particles, the crucial step in the measuring process, remained under discussion.

Until then, solid/volatile separation had been realized only under laboratory conditions using thermo-desorbers, or direct hot exhaust sampling which was incompatible with the PMP requirement to sample after CVS. The attempt to create a robust definition of a thermo-desorber led to over-extended discussions among the PMP members and threatened to slow down the entire programme considerably.
In 2003 Matter Engineering provided a solution by proposing a robust alternative, post-dilution thermal conditioning also known as volatile particle removal, VPR. Due to its simplicity in both principle and set-up, it was much easier to realize than a thermo-desorber, and thus enabled the PN principle on a regulatory level.
In 2004, Matter Engineering and TSI provided the first "Golden Instrument" to PMP, and within only 7 more years, the measurement of solid particle number concentration became an integral part of European vehicle type approval legislation.

Golden Instrument 10th Anniversary

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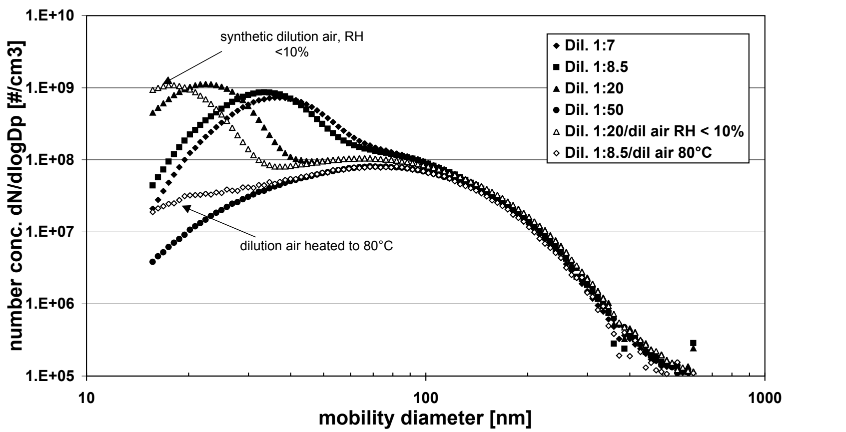
In 2013 it is 10 years since the Volatile Particle Remover was filed for patent. So it is time to celebrate the 10th anniversary of this PN enabling technology, as well as to highlight and critically review its specifications.

The key aspects are:
- The definition and operational parameters of the VPR
- The motivation for integral PN measurement without size resolution
- The choice of the lower cutoff diameter at 23 nm

Condensation of Volatiles in a Dilution Tunnel

EURO III passenger car engine on test bench / SmartSampler / fuel EN 590 < 350 ppm S



Matter Engineering AG (2000)

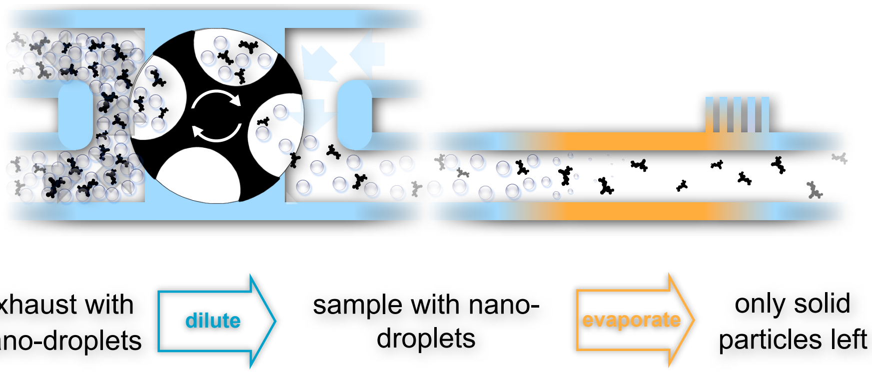
Ma, 06.08.2000, Dil_Influence_SMPS.xls, Diagr. 1

Meas. FH Biel-Nidau of June 00

In the 1990 almost every study of diesel exhaust included an investigation of the particle number size distribution. Typically, the distributions featured a bimodal shape, with the peak at small diameters exposing a rather uncontrollable behavior. This resulted in the general perception of particle number being an unpredictable, unreliable metric.
A systematic investigation of the phenomenon demonstrated the strong - and rather exclusive - dependence of the nucleation peak on dilution parameters during the sampling process (Matter Engineering, 2000). Exhaust from a Euro 3 passenger car engine, operated in steady state, was shown to produce a variety of particle distribution shapes when the dilution parameters - dilution factor, temperature and relative humidity of the dilution air - were changed. Obviously, those "particles" were formed by nucleation of vapors into nano-sized droplets during the sampling process.
Prof. Dave Kittelson commented the situation with his famous quote, "tell me which size distribution you want your engine to produce, and I will measure it for you!"

Combine Diluter+Heater to Remove Droplets from Aerosol Sample

US Patent 7,682,426



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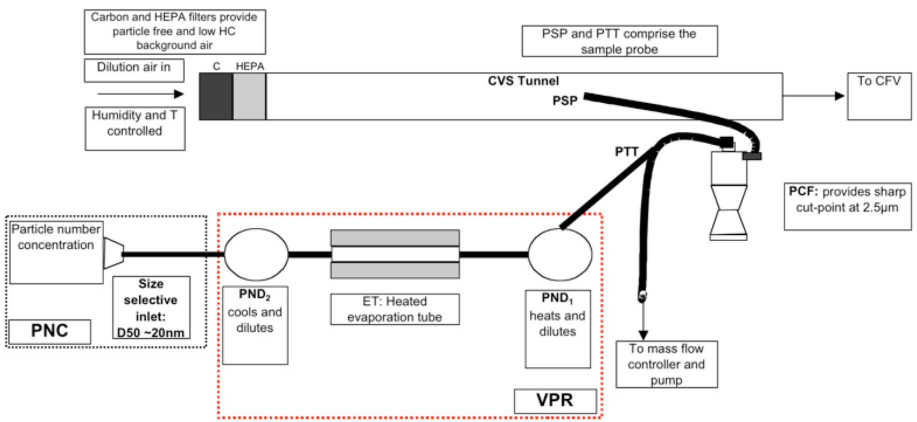
The conclusion was to exclude volatile material from the measurement and focus on solid particles, in order to obtain a repeatable and reliable result. Technically this was obtained by removing the volatile material with a thermo-desorber, a heated section followed by a activated charcoal to which the volatile material adsorbed. However, while the thermo-desorber is a useful conditioning unit for laboratory use, it is not robust enough for regulatory type approval applications. Especially the saturation of the activated charcoal after a certain period of operation is difficult to detect while it can dramatically affect the desorption performance.

A sampling set-up which overcomes the disadvantages of a thermo-desorber is post-dilution thermo-conditioning, i.e. a diluter - optionally heated - followed by an evaporation tube (Matter Engineering 2003).

Euro 5b/VI Set-up for Particle Number Count



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Post-dilution thermo-conditioning was readily adopted by PMP as Volatile Particle Remover VPR. The VPR ensures that the exhaust sample provided to the CPC contains only solid particles.

Today it is the core component of the PN measuring apparatus for vehicle type approval.

VPR - Original Challenge and Purpose

- focus on solid particles
  - **depend on engine condition and filter quality**
- evaporate sulphuric acid, water, hydrocarbons
  - **PN(volatile) depends on laboratory conditions (DF, RH, T etc.)**
- volatiles dominated by H_2SO_4 aq **-> ET Temp. ~300 ˚C**
  - **EN 590: 350 ppm S in fuel**
  - **experience mainly from VERT filter test**
- CVS favours nucleation **-> use VPR for PMP**
  - **active volatile removal needed, if sample taken after CVS**

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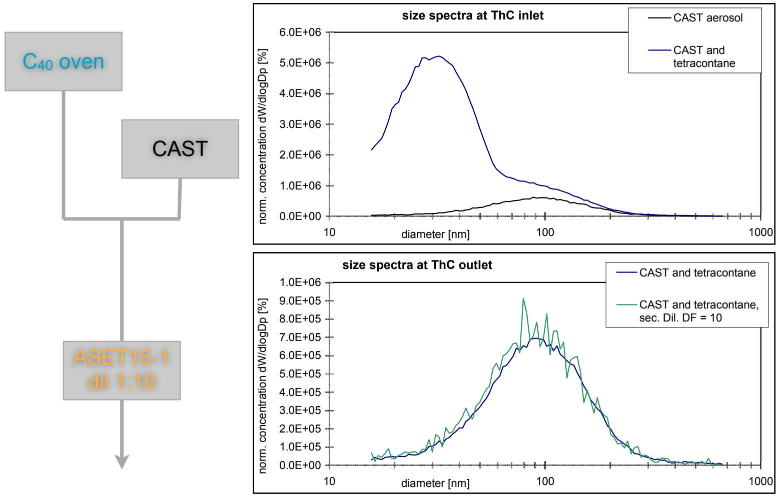
The specifications of the VPR are based on exhaust properties encountered in the late 1990s. At that time, the fuel contained up to 350 ppm sulfur, after a reduction from 500 ppm only few years before. Hence, volatile exhaust components were dominated by sulphuric acid and water, and those were most important to be removed from the exhaust sample. During the development of the VERT filter test it was found that in a temperature window from about 250˚C to about 400 ˚C the volatiles could be reliably removed while the solid particles showed no measurable change. Based on this experience the VPR evaporation temperature was set to 300˚C.
In the VERT test, where exhaust was sampled hot directly from the tailpipe, the VPR was a mere safeguard against occasional nucleation. In the PMP application, however, samples were taken post-CVS where they contained a volatile particle fraction in the majority of cases. In this application, the VPR became a mandatory functional element.

Volatile Particle Removal by Thermal Conditioner

CAST soot mixed with Tetracontane ($C_{40}H_{82}$) droplets



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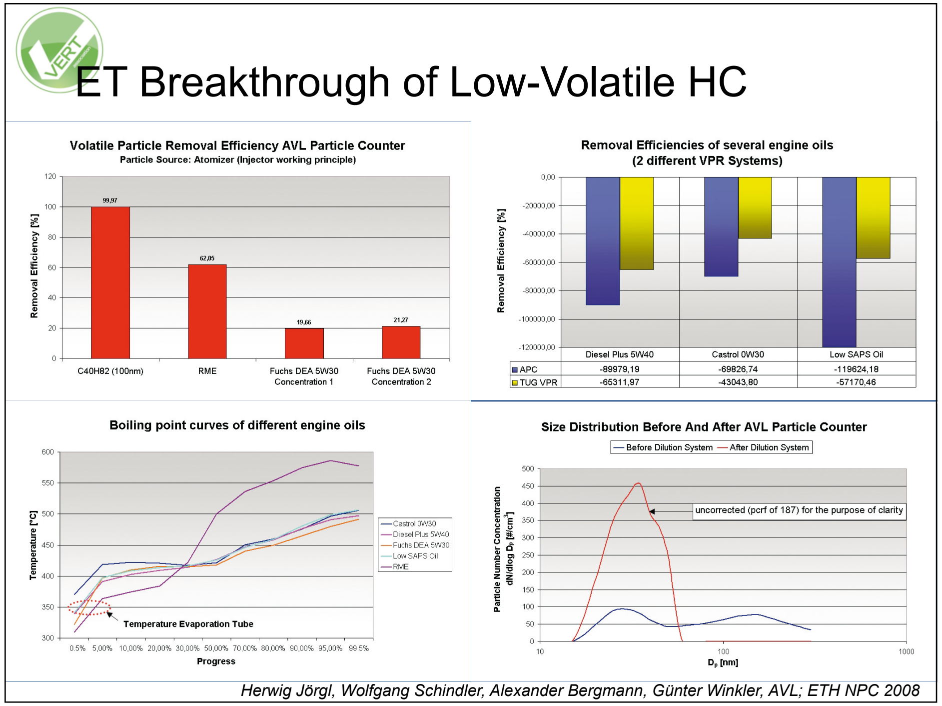
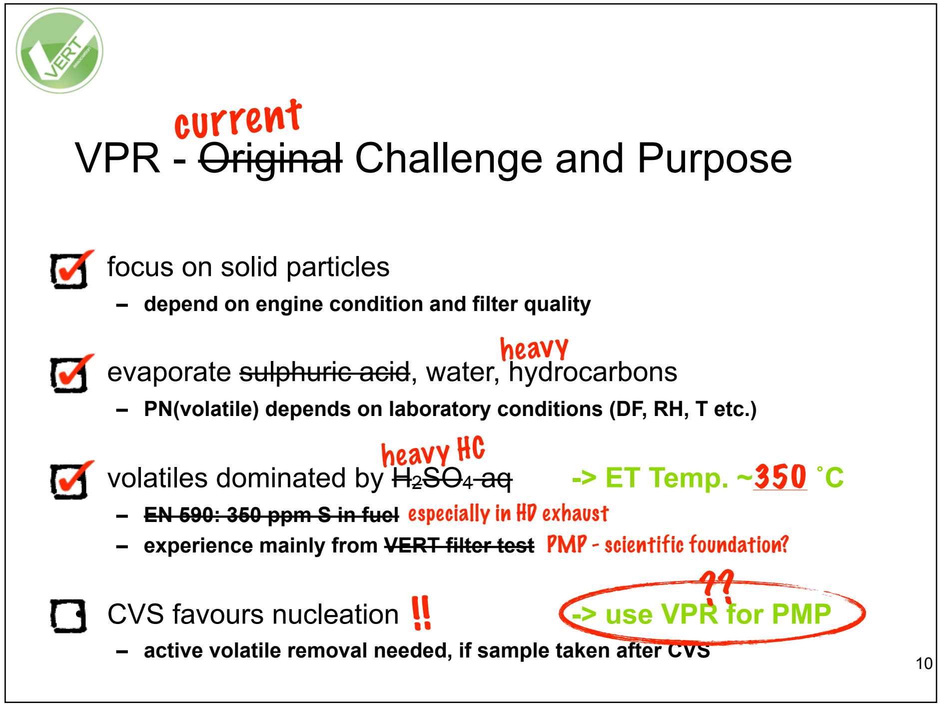
Matter Engineering (2004)

In order to prove the volatile removal performance of the VPR, tetracontane was defined as the test aerosol. Tetracontane is the C40 alcane and represents the prevailing components of lubrication oil.
The C40 aerosol can be mixed with soot from a flame soot generator (CAST) to form a "post-CVS model aerosol", featuring the well-known bimodal size distribution with a nucleation peak at some 30 nm average diameter (C40) and a soot peak at 100 nm.
Challenged with this aerosol, the VPR readily removes the volatile C40 part, while transferring the solid soot particles without changing the shape of their size distribution (Matter Engineering, 2004).



A general concern about the VPR is the potential breakthrough of volatile material. This happens if the dilution factor used in the dilution unit is too low with respect to the volatility of the component to be removed. So while sulphuric acid and most hydrocarbons may be readily removed using a dilution factor of about 15, this may not be sufficient in the case of very low volatile lube oil components.
Such a case was presented by AVL in 2008. Evaporation of several important exhaust components was shown to be incomplete, resulting in the formation of high numbers of re-nucleated oil droplets at the end of the VPR unit. The re-nucleated droplets contribute to the PN value measured downstream of the VPR and distort the measurement.
This phenomenon is particularly serious since the substances investigated are quite frequent in the exhaust of modern HD engines.



Considering today's boundary conditions, a few corrections have to be made to the original requirements and specifications of the VPR.
Volatile particle removal as such is still an essential requirement and may even be extended to new applications such as ambient air monitoring. However, the substances that challenge the VPR have changed. Modern engine exhaust contains more low-volatile, heavy hydrocarbons and less sulphuric acid thanks to the near elimination of sulfur in the fuel. In response, the temperature of the evaporation tube is now set to 350˚C. Unfortunately, the definition of this temperature is the result of merely averaging the ET temperatures of several commercial PMP systems. A more scientific foundation of the heating temperature, e.g. based on new measurement results or even toxicological data would be highly desirable.
Finally, while volatile particle removal remains a core feature of the PMP method for PN measurement, the question may be raised whether the current design of the VPR is still the best solution.

VPR: Alternative Solutions

- catalytic stripper (D. Kittelson / M. Twigg / I. Khalek)
- hot sample (e.g. Pegasor)
- in-situ measurement (e.g. LII)
- hot sampling (w/o CVS-induced nucleation)

➡ reconsider when regulating PN-PEMS!

Alternatives to the VPR have been around for some time. The catalytic stripper (Kittelson, Twigg, Khalek) removes hydrocarbons more effectively than the VPR due to its catalytic activity. Certain measuring methods can be applied to the hot exhaust without dilution (e.g., Pegasor) or even in-situ (e.g., Laser Induced Incandescence, LII). Direct sampling of hot exhaust, avoiding the CVS tunnel and the extensive nucleation occurring there, might be adopted from VERT.
The ongoing discussion about inclusion of PN into the PEMS methodology is a good opportunity to reconsider the method and technology applied for volatile particle removal.

Golden Instrument 10th Anniversary

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- Volatile Particle Remover VPR

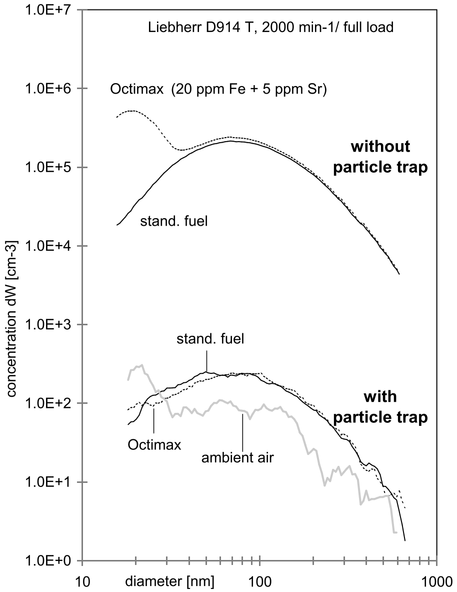
- reconsider alternatives when drafting PEMS regulation
- provide sound basis for ET temperature

- Particle Number Count without Size Resolution
- Lower Size Cut-Off at 23 nm

PMP requires an integrated measurement of the particle number in the size range 23 nm to 2.5 μm, without further size resolution. This decision was taken early on and in full awareness of sizing methods which were commercially available at the time.
In this aspect, PMP deviated from VERT, from where it had adopted its key principles.

VERT Filter Test

- size resolved PN measurement
- assess filtration efficiency, especially in critical range 200-300 nm
- stationary test points

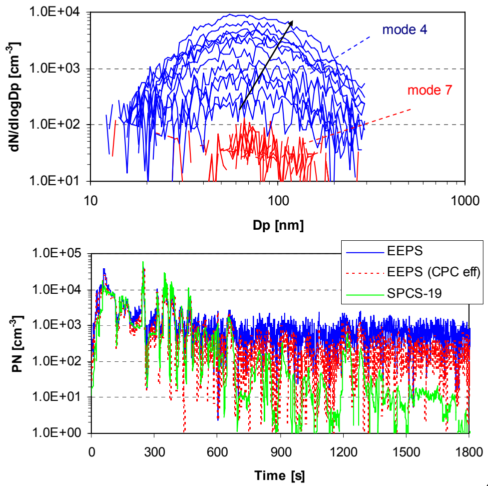


Filter: CORNING, Fuel-borne Catalyst: Octimax

The VERT filter test qualifies filter materials by their ability to remove solid particles from the exhaust gas. Filtration mechanisms and filtration efficiency vary with particle size, and especially in the transition regime between diffusion filtration (small particles) and impaction filtration (large particles) filters often show a pronounced efficiency gap. This gap usually occurs between 200 nm and 300 nm, close to the maximum of a typical Diesel particle emission.
In order to properly qualify the tested filters, the VERT protocol applies size resolved particle measurement. Filters are required to meet strict performance criteria even in their weak points, i.e. in the transition regime. More than 60 VERT-certified systems demonstrate that 99% or better filtration efficiency are state of the art.
VERT uses stationary engine operation points for the filter test, since it is sufficient to challenge a filter with high exhaust volume flow; transitional operation does not challenge the filter any further and will not provide additional information about its performance.

Adding Time Resolution to Size Resolution

- instrumentation exists and is applied in research work e.g. EEPS
- "too much data"
- type approval: measuring effort vs. result ("pass/fail")?



Giechaskiel et al. 2008, PMP-HD Exploratory Work at JRC

Other than VERT, PMP requires time resolved measurement during test cycles (NEDC, ETC). During the research works at JRC for adopting light duty PMP to the requirements of heavy duty type approval, particle size distributions were recorded at high time resolution.
While this is an interesting option on research level, it proves far too complex to provide sufficient robustness for regulatory purposes. Furthermore, the gain of information from size resolved measurement is too little to justify the additional effort in data analysis.
Therefore, it seems reasonable to keep with integral PN measurement for the sake of simplicity.

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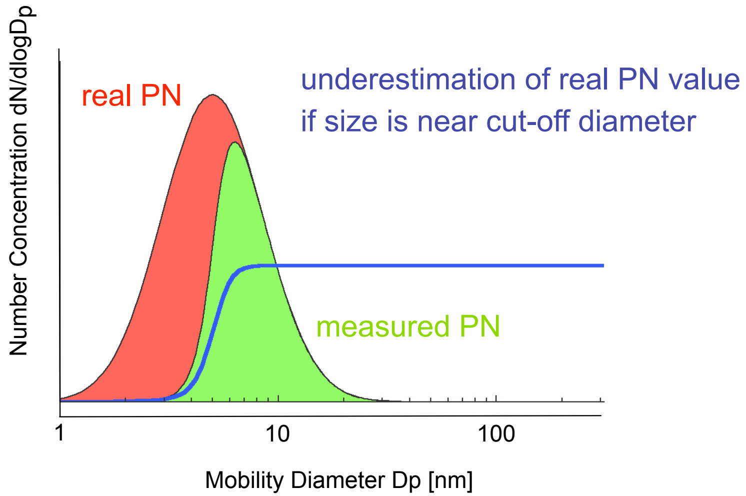
keep total PN for sake of simplicity

- Lower Size Cut-Off at 23 nm

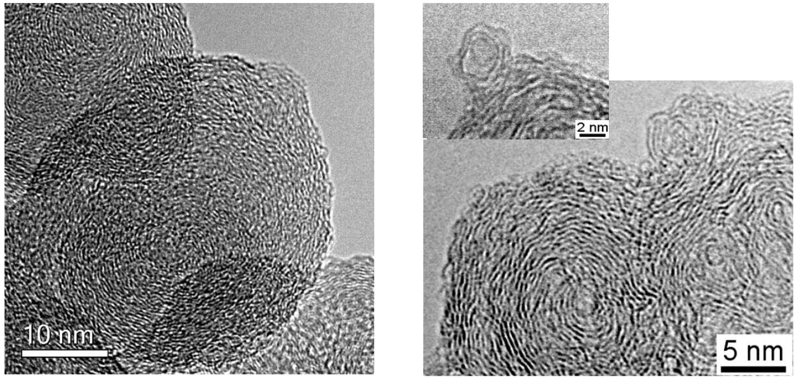
A final PMP feature to be discussed is the lower cut-off size of the particle counter at 23 nm.
CPCs used in early PMP studies worked with a size cut-off at 10 nm. PMP decided to deliberately "deteriorate" CPC performance to 23 nm cut-off in order to add further robustness against volatile particles: Should volatiles break through the VPR, they would do so by re-nucleating into sub-20 nm droplets. By excluding those from the measurement with a cut-off above 20 nm, an additional safeguard against instrument underperformance was created. (The exact value, "23" nm, was chosen due to actual CPC instrument parameters).
An additional reason for choosing a cut-off diameter above 20 nm was the objective of PMP to measure carbonaceous Diesel soot. Primary particles in Diesel agglomerates of pre-2000 engines used to be about this size, so it did not make sense to include smaller diameters.

CPC 23 nm Size Cut-Off



The exclusion of sub-23 nm particles has been the subject of discussion for several years now, especially in contributions from the US. In the current PMP setting, these particles will be vastly underestimated, if measured at all.
Recent findings corroborate the existence of significant solid PN contributions in the sub-23 nm range which, on top of being small, are suspected to be of major health concern, too, namely: smaller primary particles; metal ash particles; particles from gasoline engines.

Primary Particle Size Decreases

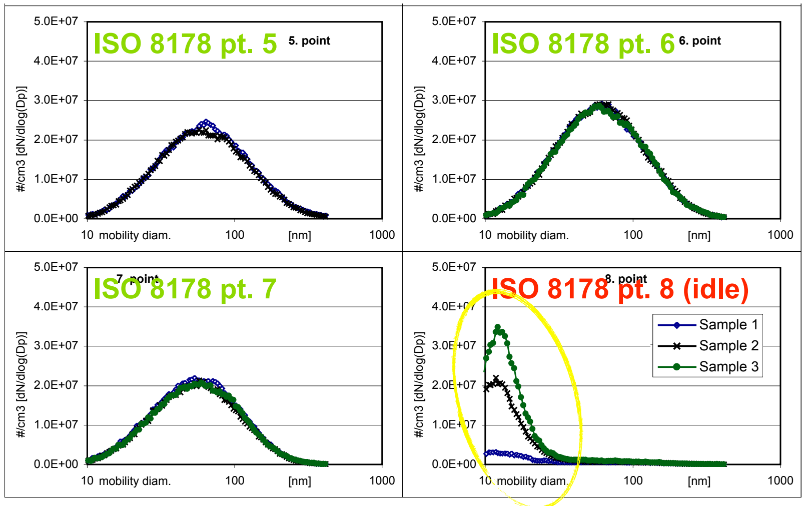


Euro I: **30-40 nm** Euro IV: **10-15 nm**

Su, D. S.; Serafino, A.; Müller, J.-O.; Jentoft, R. E.; Schlo,gl, R.; Fiorito, S. (2008) Environ. Sci. Technol. 42

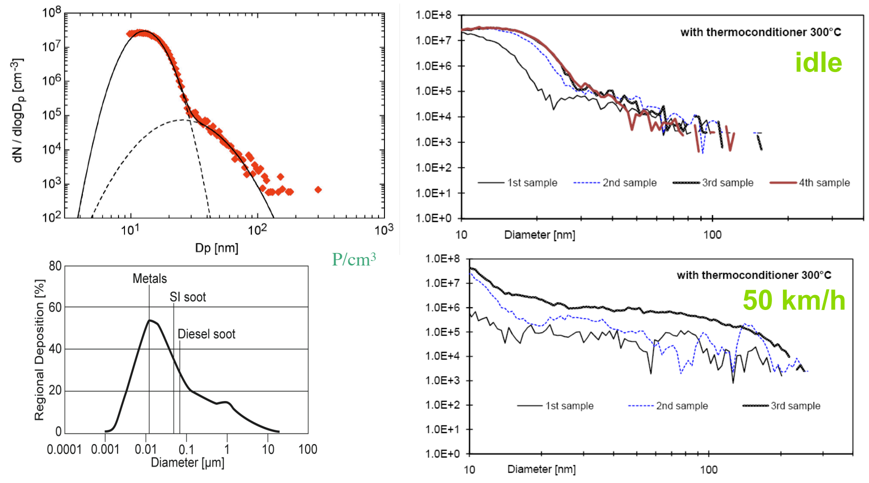
Su et al. (2008) found strong evidence of decreasing size of primary particles as engine technology advances. This is in line with expectations due to increased fuel injection pressure. Furthermore, the Euro IV soot particles expose small extensions which may be of special concern to human health.

Metal Ash Nanoparticles



Another hot topic are metal ash particles from the combustion of the lube oil film on the cylinder wall. This effect is more pronounced in low-pressure operation points (e.g., idle) since more lubricant gets from the crankcase into the combustion zone of the cylinder. A test series with the Liebherr engine in the Biel laboratories shows a steady increase of small, solid particles as idle operation proceeds.
In other engine operation points, the effect is not visible, but metal ash particles are still suspected to be formed. As there is more soot is available, they attach to the soot matrix rather than forming a peak on their own. However, as part of the soot particle they may still cause considerable, yet currently unknown health damage. Currently, lube oil, other than fuel, is not subject to any regulation, and the choice of metal additives depends only on operational, chemical performance of the lubricant.

Honda 450 Motorbike (10‘000 km)
Small (Metal) Particles from Gasoline Engine



Small solid particles, probably including metal ash, are also emitted by all kinds of gasoline engines.
Traditionally, particle emissions from gasoline engines were not regulated, not even measured, because of the very low level in terms of particle mass. Since the introduction of PN, however, gasoline engines have been shown to emit significant numbers of the smallest and most dangerous particles.
Direct injection engines will be included in PN regulations with Euro 6, but it should be considered to extend PN limits to all types of internal combustion engines.

Solid Exhaust Particles < 23 nm

- metal ash (all IC engines)
- gasoline engine emissions
- decreasing primary particle size (Diesel)

➡ reconsider 23 nm cut-off diameter!

In summary there are three groups of sub-23 nm particles which call for a revision of this large cut-off diameter:
- metal ash particles from lube oil combustion, occurring in all types of internal combustion engines
- particle emissions from gasoline engines
- decreasing primary particle size as engine technology advances

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- Volatile Particle Remover VPR
  - reconsider alternatives when drafting PEMS regulation
  - provide sound basis for ET temperature
- Particle Number Count without Size Resolution
  keep total PN for sake of simplicity
- Lower Size Cut-Off at 23 nm
  reconsider. small particles have gained importance

After ten years of investigations and operation of the Volatile Particle Remover, the following recommendations can be made for the PMP measuring apparatus:

- reconsider alternative technical solutions for volatile particle removal; the new PEMS regulations offer a good opportunity for such a revision
- provide a sound scientific basis for the heating temperature applied in the evaporation tube; 350˚C seems reasonable, but the rationale is lacking empirical foundation
- keep integrated PN (without size resolution) for the sake of simplicity
- reconsider the lower cut-off diameter, since emissions of small particles have gained importance

Golden Instrument 10th Anniversary

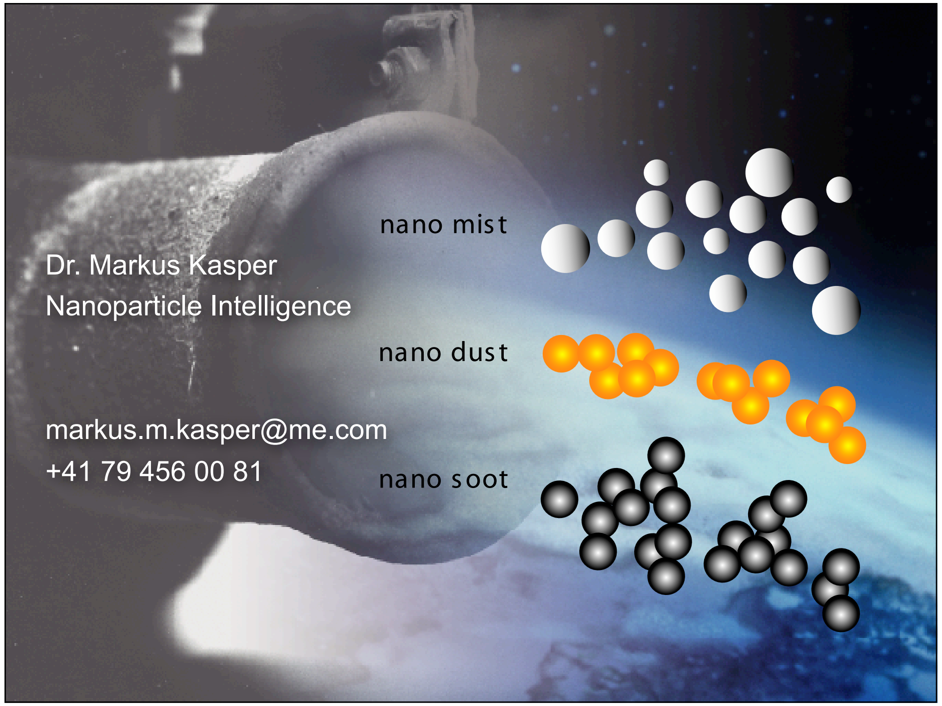
Conclusions

- PN based legislation is a fact
  - **successful standardisation of a challenging metric**
  - **PM may become obsolete**
- Things to keep
  - **ET temperature (350 ˚C)**
  - **integrated PN w/o size resolution**
- Things to reconsider
  - **reference cut-off at lower diameter (< 23 nm)**
  - **alternative VPR technologies**
- Where to go next
  - **PEMS, Inspection & Maintenance, field check**
  - **US, Japan; off-road & on-road engines; filter certification**
  - **all IC engines, not just Diesel**

Since 2011, PN based legislation is a fact. Within less than 10 years, a most challenging metric - the number concentration of nanoparticles - has been successfully standardized on regulatory level. Since current PN limit values are about 50 times stricter than the PM limits applied in the same regulation, PM may eventually become obsolete.

Although designed along the emission characteristics of the late 1990s, the main PMP features and their technical realization are up-to-date and should be kept (focus on solid particles, ET temperature around 350˚C, integrated PN).

Other aspects are not up to current requirements and should be reconsidered, such as the reference cut-off at lower diameter (< 23 nm) and alternative VPR technologies.



While PN is now implemented in on-road type approval in Europe, there is still a long way to go to clean up the air. PN regulations must be extended to more regulatory fields (PEMS, Inspection & Maintenance, field check), to other important territories (US, Japan, China) to more engine applications (off-road & on-road engines; filter certification) - and finally, PN limits should be applied to all IC engines, not just Diesel.