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SUB-23 NM PARTICLES – DO WE NEED TO CONSIDER THEM?

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Introduction



Current State:

- The present number concentration limit with its 23 nm cutoff has been established in the framework of the PMP program for diesel powered vehicles and later extended to Gasoline Direct Injection (GDI) vehicles
- In the US only the particle mass emissions are regulated while China's latest regulation follows the European one and will also concern Port Fuel Injection (PFI) vehicles. Only solid particles are considered
- The 23nm cutoff and the limitation to solid particles have been introduced to allow a stable and reliable measurement. The main goal was to enforce particle filters.
- As most of the solid particles, emitted by diesel engines are larger anyways, the cutoff at 23 nm was not very problematic
- However, as nowadays GDIs are included the situation is different. GDI particles are smaller in size than Diesel particles. A significant part of the total particles have diameters smaller than 23 nm, the size distribution peaks in the range of 10-60 nm
- Not only for GDI, but also for CNG fueled engines and PFI engines high concentrations of very small volatile and solid particles may occur





PN of <23nm particles varies with engine technologies and fuels

- If a particle filter is installed, PN <23nm is usually less significant
- If not it can be up to 50 % for GDI and CNG vehicles.
- Cold cycles emit significantly more particles than hot cycles



Measurements with CVS/PMP on chassis dynos





New Devices:

- To decrease the cutoff robust means to measure also smaller particles have to be available. This
 includes the whole sampling and conditioning part as well as the measurement itself. A
 problem are the high losses for smaller particles in the currently used dilution/conditioning
 devices.
- In the framework of surreal 23, we developed several new devices:





New devices:

> new dilution/conditioning system, optimized for low losses. It consists of a two stage diluter (first a porous tube type, then an ejector diluter, in between a catalytic stripper, CS). A stable dilution ratio and a high penetration also for very small particles, a d_{50} of 7.7 nm, is reached







New devices:

- Based on the 'automotive partector' by naneos a diffusion charging device (ICAD) has been developed, d50 = 10nm
- > Can be heated up to 180°C: no or only a very small dilution,. significantly reduced losses for very small particles, facilitates particular for RDE applications.
- > Right now research prototype.









New devices:

> ICAD vs Horiba comparison for RDE, Averaged data







New devices:

- Starting from a commercially available HM-DMA we managed high resolution in extended sub-23nm particle size range (5–30 nm)
- Accurate hot operation up to 200 C (Measurements with a single hot dilution stage)
- > Fast response time down to **1s** for the extended size range









Tailpipe versus CVS:

- > The PMP procedure requires a CVS system.
- > A tailpipe measurement is simpler, requires much less space and can avoid long heated sampling lines for the undiluted exhaust (up to 6m), as needed for CVS. This leads to high losses for small particles.
- > Tailpipe measurements are closer to what is really emitted in the atmosphere and closer to RDE testing.
- > A recent comparison study at JRC concludes that tailpipe measurement can be introduced in future regulation also for heavy-duty engines (Giechaskiel et al., 2019c).
- However tailpipe measurements require synchronization among concentration and exhaust flow measurements.











Composition:

- A large fraction of sub 23 nm particles are volatiles, however there is also a significant part of solid particles, consisting of soot, ash, metals.
- > Ash consists mainly of Ca, S, P, Fe, O, originating from lubricant oil.
- Munoz et al. (2018) show that the PAH content and therefore the toxicity of GDI particles is much higher compared to diesel particles, as these particles are smaller a significant fraction is in the sum 23 nm range.
- HDV: SCR system may produce high concentration of ultrafine particles, may significantly exceed the soot concentration. This effect is not observed for LDV.



Nature and occurrence of sub-23 nm particles





The particle size distribution emitted by a diesel engine using fuels with different lubrication oil concententration



Volatiles:

- > Volatiles are very difficult to measure reliable in procedures possible for type approval tests.
- The nucleation process is highly non-linear; therefore, small parameter changes can easily change the number concentration by orders of magnitude.
- Even if health effects and eventually other negative effects cannot be excluded with the present knowledge and available technology, considering limits for volatile particles cannot be recommended. However, research is needed learn more about their properties and possible adverse effects.
- Secondary aerosol (SA) is not considered at all, which makes a link from emission to ambient air concentrations difficult. There an option could be to include a reactor to induce a rapid SA formation in the emission measurement to get at least an estimate for the potential for SA formation (in the atmosphere this will depend on many parameters like solar radiation, humidity, species emitted from other sources).



- A number of recent studies show that a small fraction of particle filters is broken or manipulated.
- Already small cracks lead to an increase in the emissions by orders of magnitude.
- These few high-polluters dominate fleet emissions.
- As long as this is the case reducing the cutoff diameter or limit values for homologation does not have much benefit on what is found in ambient air. Therefore, some kind of inspection of in used vehicles is very essential.





Conclusions



General:

- We know that there may be high concentrations of particles in the size range below 23nm. Most of them are volatile, but there are also non-volatile ones (metals soot, salts, ??)
- We learned a lot about the nature of the solid particles in the framework of the current projects, less on the volatiles, but we know almost nothing about their health effects. (We know that 50nm particles are more dangerous than 500nm particles as they can penetrate cell membranes, enter into the blood circuit ...). More research is needed.
- There is strong evidence that surface has an important role for health effects (Schmid and Stöger, 2016). The contribution of <23nm particles to the surface is very small.</p>

Measurement:

- > We have techniques to reliably measure the number concentration of solid particles down to 10nm.
- > CVS could be replaced by tailpipe sampling, makes system smaller, lower cost, precision could be even higher.





Diesel Engines:

- Soon most diesel vehicles should be equipped with very efficient DPF's (eff. >99%), these filters will remove solid smaller (sub 23nm) particles even more efficiently.
- As long as the filter works properly, there is no need to care for small (solid) particles, if it does not the >23nm emission will be too high too to pass the type approval test.
- There is strong evidence that about 5% of in use filters are defect or manipulated, these high polluters dominate fleet emissions, these vehicles have to be identified and repaired, for example by periodic emission measurements. This is much more important than changing the cutoff for the type approval test.
- For diesel engines and solid particles there is no real need for a cutoff reduction (as long as efficient filters are used)



Conclusions



SI- Engines:

- GDI engines emit high concentrations of particles in the range of 10 to 40 nm, these particles therefore have to be considered.
- If equipped with state of the art GPF (as efficient as DPF) these particles will also be removed efficiently and again it makes not much difference whether the limit is 10 or 23 nm.
- However, currently used GPF often have much lower efficiencies, the contribution of <23nm particles then may be significant; this is the case where considering solid sub-23nm particles is important.
- > This becomes even more important if engine optimization enables meeting the limits without GPF.
- As high number concentrations are also observed in the emissions of PFI and CNG engines, these should be included, independently from the shift in the cutoff-diameter.
- Detection of high polluters is also important for SI-engines.



Conclusions



Final Remarks:

- It definitely is important to study sub-23nm particles, learn more and have techniques to measure/characterize them.
- For legal measurements (type approval, technical inspection) it is not urgently needed to include them, if efficient filters are used. The use of good filters can also be enforced by lowering the limit value.
- To make sure that the filters work properly a periodic emission measurement is needed (has been introduced in the Netherlands).
- Perhaps important, but for sure much more difficult is considering the volatiles (not only sub 23nm), however, not enough is known up to now (neither about health effects nor how to reliably measure them).
- For volatiles, a number concentration does not make much sense. On the one hand it strongly depends on temperature, dilution and other parameters, which makes a reproducible measurement very delicate or even impossible, on the other hand these are no longer particles as soon as they are precipitated in the lung (then chemistry and mass, but no longer size and number are essential).







