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MINUTES OF 26TH PMP IMFORMAL GROUP MEETING

1. The 26th PMP meeting was held on 6th December at JRC in Ispra. This note records the key points from the discussions and presentations in the meeting.

VPR Calibration Round Robin

2. JRC presented the background to and current status of the exercise. Golden VPR, PNC and (graphite, spark) Aerosol Generator were being circulated to participating laboratories. Each lab was measuring gas dilution factors and PCRFs at 30, 50 and 100nm aerosol sizes using the Golden PNC and Aerosol generator and their own equipment. As an option labs were asked to check PNC linearity and measure PCRF at 15nm aerosol size.

3. Eight of ten labs have now completed testing and the following aerosols have been used; diesel exhaust, CAST, mini-CAST, NaCl, Palladium. This includes testing with polydisperse aerosol at Empa and with & without neutraliser at Horiba. The Round Robin is expected to conclude by the end of February 2012. **Participating laboratories were reminded to submit their results to JRC as soon as possible**, including raw measurement data, a schematic of the equipment set-up and a 3-4 page description of the measurements taken.

4. Horiba presented their experience from the Round Robin. They noted that they initially tried PCRF measurement with polydisperse aerosol, but had experienced significant problems with this and not pursued it. Using a 23nm D_{50} PNC they found substantial variation in 30nm PCRF across three different aerosol generators (NaCl nebuliser, mini-CAST and graphite spark), with only the (Golden) graphite spark generator giving plausible results. The implausible PCRF results for 30nm particles may have been due to the combination of the low VPR downstream particle concentrations, being on the steep part of the PNC cut-off curve and some material dependency in the PNC cut-off.

5. Matter Engineering noted that the mini-CAST generator might be producing significant concentrations of volatile particles which were not fully removed by thermal conditioning before the VPR inlet. Professor Kittelson commented that some generators produced very highly charged aerosol, although Horiba noted that, in this case, the results with and without a neutraliser were similar. Using a 2nm D_{50} PNC all aerosol generators gave similar PCRF results (+/-5% CoV), again the neutraliser appeared to have no impact on the measurements. TSI commented that particle losses for the Golden VPR design were not very size specific reducing the effect of the neutraliser.

6. Horiba showed data on the (size classified) aerosol stability over time for the different aerosol generators. The NaCl nebuliser generator produced very stable

concentrations at all three aerosol diameters used for VPR calibration. The mini-CAST generator was fairly stable at 30 and 100nm, but showed substantial variation at 50nm. The spark generator concentrations varied by around +/-1000cm^{-3}, from mean concentrations in the 5000-9000 range (depending on aerosol diameter). TSI noted that it was best to keep the DMA inlet concentration in the 10^6-10^7 cm^{-3} range.

7. AVL also presented their VPR calibration experience using thermally treated CAST aerosol, a neutraliser and a 10nm D_{50} PNC. They found $PCRF_{av}$ repeatability to be +/-6% (2σ) for normal PCRF settings, this included measurements taken on units after 11 months in service. They did however note that repeatability became significantly poorer at PCRF settings above 2000. This was attributed to downstream aerosol concentrations at high PCRF settings being very low. The chairman noted that the PMP roadmap calibration work in 2007 had also seen poorer calibration repeatability at high PCRF settings for this reason. Scania noted that they had seen poorer repeatability at PCRF settings of 2000, AVL suggested that if PRCF was outside of +/-10% at PCRFs of up to 5000 then this was indicative of a problem with the unit. Horiba noted that their system operated at PCRFs up to 3000, for raw exhaust measurement they used an additional, separately calibrated diluter.

PNC Calibration & Stability

8. JRC presented their experience of calibrating the Golden PNC used in the VPR Round Robin exercise. They used a tandem DMA set-up in order to enable double charging of particles for the purpose of extending electrometer calibration range to sub 1000cm^{-3} concentrations. With double charging and a fivefold increase in electrometer flow rate they extended electrometer measurements down to a concentration of 300cm^{-3}. However they found discrepancies between simulated and measured post DMA concentrations of 10-14% suggesting uncertainty into these measurements.

9. JRC also calibrated against a reference PNC using spark generated graphite aerosol and evaporation-condensation generated emery oil aerosol. They found lower counting efficiencies for graphite particles even above the D_{90} diameter and that the difference relative to emery oil measurements increased as the PNC evaporator temperature delta was reduced. VW and TSI expressed surprise at this, not having seen counting efficiency above the D_{90} diameter to be aerosol material dependent in their own measurements. Horiba queried whether this might be a concentration effect, JRC responded that that had seen the same effect at different aerosol concentrations. TSI queried whether the experiment had been repeated with the positions of the two neutralisers reversed, JRC indicated that they had not, but had seen the same effect with a range of different neutralisers. JRC suggested that the graphite aerosol generator might be producing agglomerates, which TSI agreed could have an influence.

10. AVL presented their experience from calibration of over 40 PNCs. They found some non-linearity of PNC response, but only +/-3%. In line with other investigations they also found different cut-off counting efficiency for CAST compared to emery oil particles. Most significantly they found the counting efficiency of a significant number of PNCs had degraded after 1 year, although some of these had been used for raw exhaust measurement, rather than solely for regulatory measurement. They however found that counting efficiency was restored when the PNC wick has changed. TSI noted that they now recommend

changing the wick every 6 months as part of routine maintenance. VW commented that they had not seen this to be necessary in their experience.

11. Scania presented information on problems they had experienced with 4 PNCs failing calibrations on both slope and cut-off performance. All had lost a significant proportion of their counting efficiency. Scania are now instituting routine PNC wick replacement and using purer butanol in an attempt to address this issue. They are also conducting comparisons between measurement PNCs sampling the same CAST or ambient aerosol.

12. Reasons for PNC counting efficiency deterioration were discussed. TSI commented that this was more prevalent in heavy duty testing and was probably due to reaction of acidic components in the exhaust gas and butanol contaminating the PNC wick. JRC were examining whether use of a Catalytic Stripper instead of a VPR would help prevent this. Ricardo expressed doubts about this if organic acids were the problem. Professor Kittelson noted that it could be related to sulphuric acid formation, which would be consistent with the problem being more prevalent in heavy duty engine testing. AVL noted that they had found presence of butyl esters in their analyses and also that it would be worth investigating urea effects as Scania's experience was with post SCR exhaust.

European Metrology Research Programme

13. METAS gave a presentation on the European Metrology Research Programme project to develop an international standard for automotive PNC calibration and protocols for calibration aerosol generation. The project plans to deliver recommendations on size standard aerosol for PNC calibration by May 2012 and is examining Au, Ag and PSL aerosols with generation from suspensions. The project plans to deliver recommendations on temperature resistant aerosols at 30, 50 and 100nm sizes for VPR PCRF linearity calibration by November 2012. The project plans to deliver recommendations on "soot-like" aerosols for PNC cut-off checks by May 2013.

14. Some reservations were expressed about the suitability of Ag particles for cut-off checks and potential future use with water based PNCs.

15. Task 2 of the project aims to develop a standard for combustion particle number concentrations. National standards are to be delivered by November 2013, there will then be an international comparison exercise. By May 2014 the project aims to complete an international round robin exercise of comparative PNC calibration.

16. JRC indicated that they were involved in the project and METAS agreed to act as a contact point to feed in experience from PMP informal group members to the project. METAS agreed to provide the group with an update on progress of the project at a future PMP meeting.

Measurement of sub 23nm Particles

17. Professor Kittelson gave a presentation on solid particle measurement from a number of studies, in particular recent research with the University of California Riverside.

18. He noted that most penetrating particle size for DPFs is around 300nm, so limits controlling >23nm particles are expected to be effective in controlling emissions of all particles. However, for non-DPF equipped diesel engines significant concentrations of sub 10nm ash particles are produced at idle conditions. For petrol engines, significant sub 23nm particle concentrations were observed on PFI

engines using fuels with metallic additives, and measurements at SWRI showed around 20% of solid particle concentrations from GDI engines to be in the 10-23nm size range. Solid particle emissions for HCCI operation were seen to be entirely in the sub 23nm size range.

19. Measurements with University of California Riverside's on-road mobile lab had shown unexpectedly high concentrations of sub 23nm particles in post DPF exhaust at high loads. Post VPR measurements at high load with using 23nm, 10nm and 2.5nm cut-size PNCs suggested no particles were present in the 10-23nm size range, but there were substantial post VPR concentrations in the 2.5-10nm size range. Measurements using a Catalytic Stripper also initially showed no particles in the 10-23nm size range and initially no particles in the 2.5-10nm size range. However over prolonged sampling particles in the 2.5-10nm began to appear downstream of the Catalytic Stripper also. At lower load much lower particle concentrations were observed. Post VPR measurement showed no particles in the 10-23nm size range, but presence of particles in the 2.5-10nm range. However, measurements downstream of the Catalytic Stripper showed little evidence of particles in the 2.5-10nm size range. CVS measurement with no VPR showed lower concentrations suggesting formation of particles within the VPR.

20. Laboratory experiments with Thermodenuder and Catalytic Stripper showed the Catalytic Stripper to be significantly more effective at removing heavy hydrocarbon and sulphuric acid particles. They also suggested some evidence of formation of particles by the Thermodenuder.

21. In conclusion Professor Kittelson noted that for engines equipped with DPFs regulating for >23nm particles effectively controls all solid particle emissions. However for non-filter equipped engines there can be substantial concentrations of sub 23nm solid particles. Extending the regulatory particle number measurement technique down to a 10nm cut-off size would be problematic with the current VPR due to nucleation of semi-volatile (sulphuric acid) particles, but a catalytic stripper would be an efficient means of conditioning the sample to eliminate formation of these particles. Extending the measurement below 10nm would be extremely problematic as nucleation of sub 10nm particles was seen downstream of both VPRs and Catalytic Strippers and there was some evidence of VPR and thermodenuders creating solid particles in this size range.

22. Dr Mayer gave a presentation on TTM's work on nanosize metal oxide particle emissions. He noted that peak penetration of particles into the alveoli occurred at 20nm size and that peak penetration of the bronchial tract was at sub 10nm size and commented that it was unclear whether particles deposited in the bronchial tract were captured and released or may travel via the olfactory nerve to the brain.

23. Data on toxicity for different compounds showed Copper, Zinc and Iron oxides exhibiting higher toxicity than Carbon. Engine wear, lubricating oil, additives and catalyst coatings were all potential sources of metallic compound particles. TTM had conducted mass spectrometry measurements on particles collected on ELPI impactor stages. For a non-DPF diesel, size distribution measurements showed a peak particle concentrations at around 20nm under engine idling conditions, where significant lubricant burn can occur. Spectrometry of the material collected on the ELPI (<30nm) back-up stage at idle showed significant quantities of Calcium, Iron and Zinc. With an Iron fuel-borne catalyst, mass of iron in the engine-out particulate increased 30 fold, although a DPF proved almost 99% effective at

capturing this material. Further VERT measurements confirmed that DPF filtration efficiency is excellent even for sub 30nm particles.

24. Measurements on a range of petrol engined vehicles showed an old car and a motorcycle to have significant particle concentrations in the sub 23nm size range. A more recent port fuel injection (PFI) car exhibited much lower concentrations, as did a recent scooter at idle although at 50km/h it exhibited similarly high concentrations to the old car and motorcycle. Total particulate emissions included significant quantities of Calcium and Zinc in particular.

25. Dr Mayer concluded that engine wear and lubricant oil consumption produce significant quantities of metallic particles of around 20nm size in the case of both petrol and diesel engines. These particles are likely to have higher toxicity than soot, but are efficiently removed by DPFs if these are fitted.

26. JRC presented the results of a recent measurement programme on sub 23nm particles. Their work involved using the current VPR specified in Regulation 83 with a range of PNCs with 4.5, 10 and 23nm D_{50} cut sizes. They had tested 3 GDI, 2 PFI and 2 DPF vehicles (including measurements on a Flex Fuel GDI running on E85 and a bi-fuel PFI running on CNG) over cold start NEDC and hot start CADC cycles.

27. NEDC results suggested 10-20% of post VPR particles were in the 10-23nm size range for GDI vehicles, 35-56% for PFI and (surprisingly) 26-45% for DPF vehicles. Measurements using the 4.5nm cut size PNC were higher for all technologies, but not significantly so. Results on the CADC Motorway cycle gave slightly higher proportions of post VPR particles in the 10-23nm size range, but much higher for the 4.5nm cut size PNC in some cases. However 4.5nm measurements were found to be sensitive to PCRF setting (higher settings giving much lower particle concentration measurements) suggesting volatile material in this size range was penetrating the VPR.

28. Active DPF regeneration measurements on the CADC cycle showed an enormous increase in volatile particle concentrations, but post VPR concentrations (with all PNCs) were also increased by more than 2 orders of magnitude. Again 4.5nm cut size PNC results were sensitive to PCRF setting, suggesting volatile particles in this size range are penetrating the VPR.

29. JRC confirmed that the DPF vehicles tested were fitted with catalysed DPFs. Professor Kittelson commented that the post DPF sub 23nm particles were probably volatile particles (e.g. condensed sulphuric acid). VW asked if JRC had made any measurements with a Catalytic Stripper (which would be more effective at removing such volatile particles) instead of the VPR. JRC confirmed that they had not, but hoped to do so during the WLTP Validation 2 exercise as part of their DPF regeneration investigative measurements.

30. The chairman indicated that he would report back to GRPE on the discussions on sub 23nm particle measurement and seek GRPE’s views on whether PMP should discuss and investigate this subject further.

Heavy Duty Round Robin Status Update

31. JRC confirmed that all laboratories had completed testing with, the exception of JRC’s end of round robin testing. JRC had just received the engine for this testing. JRC noted that a number of participating labs had not yet submitted their data. **Labs were requested to submit their results, modal data and test reports** to

JRC (thanasis.mamakos@jrc.ec.europa.eu) **as soon as possible**, copying to Daimler (hj.stein@daimler.com).

Chris Parkin

PMP Chairman