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CRC-Meeting, Paris, 19.6.2000

**4th Conference on Nanoparticle Measurement
'Sampling/Measurement' Workshop
7-8 August 2000**

REPORT FROM PARIS PM WORKSHOP, 19 JUNE 2000

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Particulate Emission Workshop, Paris 19 June 2000

On 19 June 2000, a workshop on particulate emissions was held in Paris. The purpose of this workshop was not to look for new advances, but rather to summarise current activities and attempt to provide some guidance and co-ordination for future research activities. The following is a summary of the output from the meeting.

Overall

- Exhaust particles are not all the same, and can conveniently be divided into accumulation mode and nucleation mode
- Measurement of accumulation mode particles is well established
- For nucleation mode particles, formation mechanisms, measurement methodologies, and sampling conditions need more work to relate to the real world.
- Standardised measurement methodologies are desirable to enable exchange of research data and assist health experts, but we should not narrow down the range of measurements prematurely. We may need more than one type of measurement to characterise the emissions
- PM mass measurements have served us well and should not be discarded. However, traditional filter paper measurements are becoming more challenging as emission levels decrease.
- There is concern that we do not understand the health mechanisms/implications for nucleation mode particles and that new measures should not be introduced prematurely.
- Secondary particles make a significant contribution to airborne PM and should not be neglected in the pursuit of primary emissions

Accumulation Mode Particles

- Regulated PM mass emissions should be maintained while work proceeds on new technologies
- There is evidence that, for accumulation mode particles, PM number emissions decrease when mass emissions decrease
- However, filter paper measurements are becoming more difficult as emission levels decrease and improved techniques may be needed to ensure that reproducible results can be obtained
- These may include modifying the filter paper method to collect only dry soot, or substituting alternative integrated PM measurements.
- Size and number emissions can be measured reproducibly for particles in the accumulation mode range since emissions are insensitive to the sampling conditions. however there are considerable calibration challenges in adopting these measurements, and reproducibility is not as good as integrated mass measurement

Nucleation Mode Particles

- Nucleation mode particle formation is extremely sensitive to the sampling conditions. While it is possible to control sampling conditions well enough to give reproducible results, producing measurements that are relevant to real world conditions is a challenge
- This variability of nucleation mode particles extends to real world conditions. Vehicle chase experiments show a very strong sensitivity of the number of nucleation particles to ambient temperature.
- There is concern that the potential health effects of nucleation mode particles are not well understood, nor is improved understanding likely for 5-6 years.
- In developing test procedures to measure nucleation mode particles, experiments to link laboratory measurements with the real world will be important
- The complexity of the problem suggests a stepwise approach
 - ⇒ first decide on the measurement methodology
 - ⇒ then choose the sampling conditions
- At each stage, links are needed with evolving health and real world emissions knowledge.

Measurement Techniques

- Nucleation mode particles are formed from sulphate and hydrocarbon emissions, and are dependent both on the fuel properties and vehicle hardware, especially the presence of strong oxidation catalysts
- Integrated measures such as total number, surface area, mass could provide a way of characterising the particles, rather than measurement of number/size profiles
- Measurement of precursors (sulphate, speciated hydrocarbons) was suggested as an alternative, but prediction of PM emissions from these measurements is very challenging because of the strong sensitivity to conditions in the exhaust and sampling systems. Fuels and engines will be different in 2007 than today, making prediction even more difficult.

Sampling Conditions

- Nucleation mode particles are very sensitive to test and sampling conditions
- some of the observed variations are believed to be artefacts eg through adsorption/desorption of hydrocarbons from walls
- others are known to be real as shown by vehicle chase experiments
- Choosing the best test conditions and relating these to the real world will take considerable effort
- One suggestion is to take a 'worst case' sampling scheme that measures the maximum potential to produce small particles. The problem of relating these measurements to the real world would remain, however.

BACKGROUND

- **Workshop held in conjunction with 2000 CEC/SAE Spring Fuels & Lubricants Meeting, Paris, 19 June 2000.**
- **Organising bodies: CRC, CEC, JAMA, ACEA**
- **OBJECTIVES:**
 - **Provide a focus for technical discussion**
 - Review technical knowledge on exhaust particulate emissions
 - Identify gaps in our knowledge
 - Discuss need for new measurement techniques
 - . . and how to make progress
 - **Document discussion as a basis for the future**

ALL PARTICLES ARE NOT THE SAME

- Number distribution shows

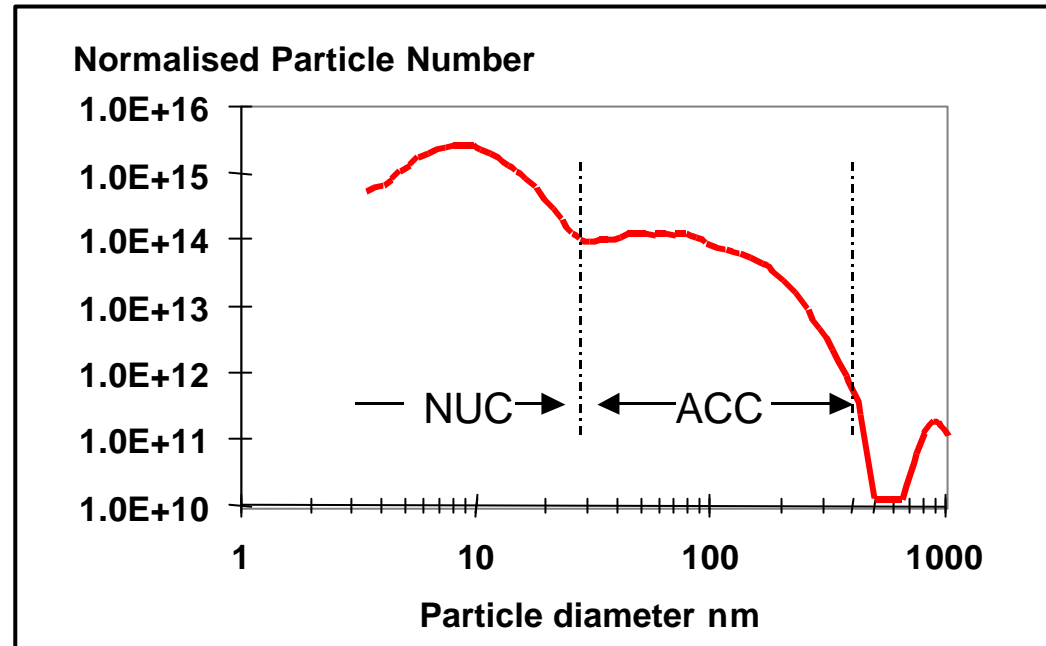
ACCUMULATION MODE

circa 100 nm
carbonaceous/HC/
sulphate

NUCLEATION MODE

up to 20-30 nm
sulphate/HC

Typical Particle Size Distribution



- Removing carbonaceous particles may increase nucleation mode through homogeneous sulphate/HC condensation

ACCUMULATION MODE PARTICLES

- **Considering only the (carbonaceous) accumulation mode particles**
 - Particle numbers tend to be lower when PM mass is lower
 - Broad trend across vehicle technologies

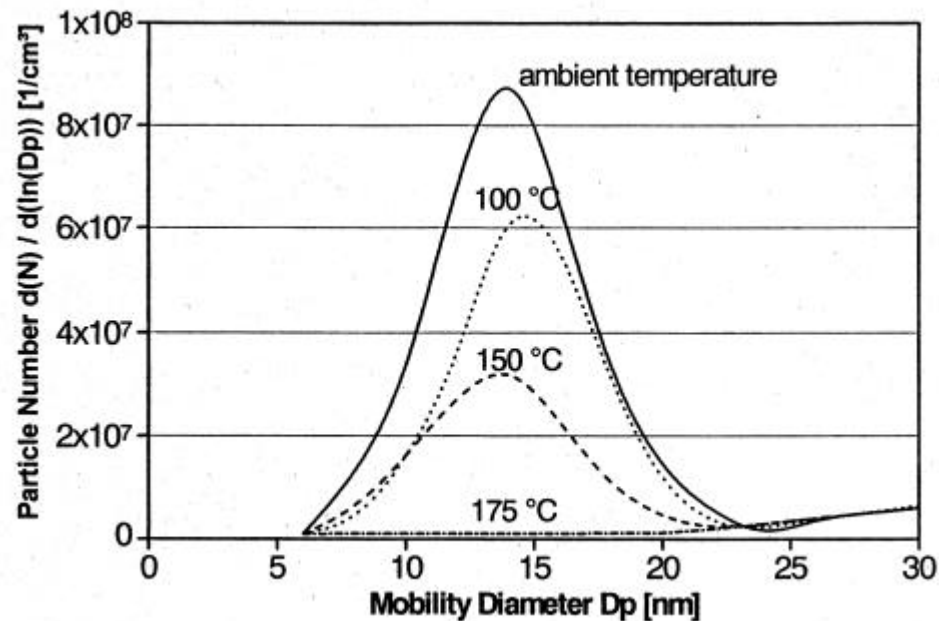
The current mass emission standards are an effective way of controlling carbonaceous PM emissions and should be retained
- **Filter paper mass measurement is still the most reproducible measure of PM mass**
 - But the cleanest vehicles are now close to the limit of detection

More precise measurement may be needed in the future

 - *Improved filter paper method?*
 - *Alternative measure?*
- **Alternatives to mass measurement should be based on understanding of health effects**

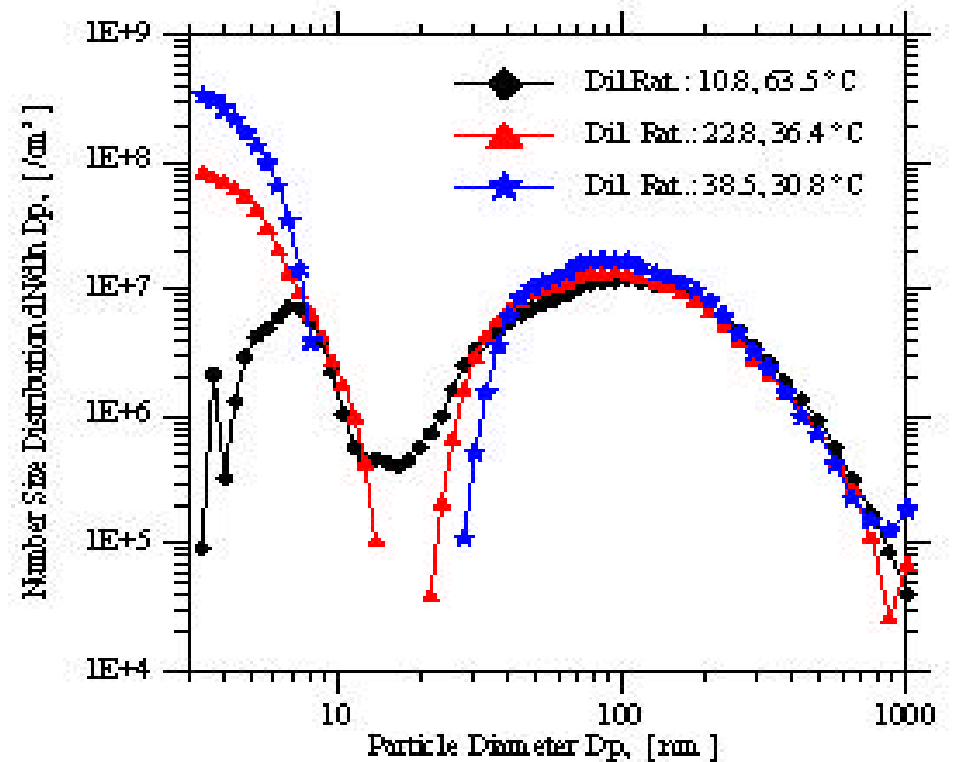
THE NATURE OF NUCLEATION PARTICLES

Nucleation particles are volatile



Source: SAE 981374; H Lüdgers, FEV

Measurements sensitive to dilution conditions



Source : Concawe

NUCLEATION MODE PARTICLES

- **Much progress in understanding, but**
 - **Health effects not well established**
 - improved understanding will take 5+ years
 - **Emissions very sensitive to measuring conditions**
 - in real world as well as in the laboratory
 - temperature, humidity, background aerosol levels
 - **Evolution of particles in the atmosphere needs more study**
 - **Secondary particles should not be neglected**
 - more important than primary emissions in some areas
- **Measurement conditions can be controlled**
 - **Reproducible results are possible**
 - ***But may not be relevant to the real world***

NUCLEATION MODE PARTICLES

- **Nucleation particle/droplet formation depends on**
 - **The fuel**
 - sulphate/HC formation in the exhaust
 - **The vehicle**
 - oxidation catalysts, needed for PM/NO_x control
 - convert SO₂ to SO₃ ==> condenses as sulphate
 - PM traps remove nucleation centres for volatiles
 - **Vehicle operating conditions**
 - exhaust temperature affects SO₃ formation
 - **Conditions in atmosphere/sampling system**
 - degree of dilution, temperature of ambient air
 - affects condensation of SO₃, hydrocarbons

WHERE DO WE GO FROM HERE?

- **Two stage approach for Nucleation Particles suggested:**
 - **Decide measurement technique**
 - Surface area better than number?
 - Integrated or size distributed measures?
 - Is particle composition important?
 - **Then decide best sampling conditions**
 - How to correlate with a variable real world
- **Links to related research are important**
 - **Health effects:**
 - Is the chosen measurement appropriate?
 - **Real world experiments**
 - Are sampling conditions appropriate?
 - How do particles disperse/change in the air?
 - **Atmospheric modelling**
 - Relative contributions of primary/secondary particles

KEY MESSAGES

- **Measurement of accumulation mode well established**
 - **Mass measurements valuable**
 - **May need some improvement as emission levels decrease**
- **We do not know how to measure the nucleation mode particles in a meaningful way**
 - **But much progress being made**
- **Secondary particles make a significant contribution**
 - **Should not be neglected in pursuit of primary emissions**
- **Standardised measurement techniques for nucleation PM desirable**
 - **To enable data exchange**
 - **To assist health experts**
 - ***But avoid narrowing the range of measurements prematurely***