Particle Measurement Programme (PMP):

Final Report of Phase 1 of Module 1: Literature Review

A report produced for DTLR

John McAughey

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Executive Summary

Context
The Particle Measurement Programme (PMP) has been initiated primarily to ensure that future stages of European vehicle emissions regulations lead to the exploitation of the full potential of particulate emissions control technology. In parallel with the simple driver to achieve reductions in total PM_{10} mass emissions, there is the additional pressure to take account of metrics most directly linked to adverse health effects.

The programme's 'core' approach is based on the assumption that the appropriate metric(s) will be applied, in the first instance, to the carbonaceous ultrafine component (accumulation mode) of the exhaust emissions since this mode appears to be both robust and reproducible. The measurement procedure should ideally be compatible with existing type approval facilities and procedures. The measurement system should ideally also be easily adapted to respond to reprioritisation of appropriate metrics as further evidence on health effects becomes available.

In the light of an initial review, which builds on recent reviews both within and outside the PMP, and the monitoring of the literature during the contract reporting period, the current status in two of the key topics, health effects and measurement, are as summarised below. In view of the relatively short reporting period, 'literature' encompasses unpublished conference proceedings and research activity as well as published papers and reports.

Whilst significant publications in the health effects field have emerged in the reporting period, much of the relevant research on measurement issues is concentrated in major ongoing project initiatives – including PMP itself.

Health effects - Epidemiology
The key research activities relate to the epidemiology of short- and long-term particle exposure, and to the potential toxicological mechanisms which may help identify key components of the ambient particle mix.

In general, health effects in epidemiological studies have been related to mass-based particle metrics (PM_{10}, $PM_{2.5}$) as these parameters are most commonly monitored in ambient monitoring networks. There are, however, some limited data on health effects related to alternative markers such as particle number or surface area equivalents. Recent re-analyses of existing data support a causal association between particles and acute mortality and morbidity, on the basis of mass-based particle markers.

For longer-term cohort-based longitudinal studies, the UK Committee on the Medical Effects of Air Pollutants (COMEAP) has concluded that it is more likely than not that there is a causal relationship between particulate air pollution and long-term health effects and that the magnitude of the long-term health effects is at least equivalent to that of short-term effects, but may be up to ten times more significant.

Thus these data reinforce the existing health-related associations against which improvements in air quality and reductions in emissions, together with associated population-based

economic benefits, are being sought. Future insights are likely to be gained from improvements in source apportionment of ambient particles being adopted in epidemiology studies.

Health effects – Toxicology
There are insufficient data to fully prioritise metrics at this time, but some general conclusions can be drawn.

- Particle mass will continue to be an important metric due to the existing associations between PM and health effects.
- Current hypotheses from toxicology studies flag the importance of ultrafine particles and metals for acute inflammatory effects through an oxidative stress mechanism.
- Elemental carbon (EC) has been identified as having long-term effects on health (lung cancer) and occupational exposure controls already exist.

Measurement, sampling and calibration issues
Detailed information on these issues is contained in the reports arising from the parallel Phase 1 technical programmes but a number of general points have been identified as follows.

- Immediate regulatory focus is on solid particles, which have proven to be robust under many sampling regimes. This simplifies sampling issues, thereby allowing a wider range of sampling options to be considered.
- Further research on volatile particles and their precursors is required before their significance in the context of future emission reductions for diesels and other combustion sources can be assessed.
- The solid particle mode can be isolated (and nucleation mode suppressed) by the use of high dilution and/or thermodenuders.
- Particle number and active surface area can be measured to high sensitivity with existing methods.
- Some mass measurement techniques under development may offer equivalent levels of sensitivity (for example, in the case of isolated nucleation mode emissions, mass can be derived from number and surface area measurements).
- Tailpipe sampling will require a measurement and calibration infrastructure for time-resolved volumetric flow.
- Existing test procedures might need to incorporate appropriate pre-conditioning to reduce tailpipe memory effects.
- Existing test procedures will need to take account of continuous and periodic trap regeneration.
- Sampling losses by impaction, diffusion, electrostatics and thermophoresis are well understood and have been minimised by the design of short, heated, electrically conductive sampling lines.
- There is an existing calibration standards capability for most of the key measurement parameters involved in the programme (particle size, mass, number, active surface, elemental carbon, volumetric flow, temperature, relative humidity) but a system for implementation on a systematic basis is not yet developed.

Contents

1 INTRODUCTION **1**

2 HEALTH EFFECTS **3**

2.1 EPIDEMIOLOGY 3
2.2 TOXICOLOGY 5

3 MEASUREMENT **8**

3.1 PARTICLE COMPONENTS 8
3.2 PARTICLE METRICS 9
3.3 SAMPLING 10
3.4 TEST CYCLES 11
3.5 INSTRUMENT SELECTION CRITERIA 11
3.6 CALIBRATION 12
3.7 CONCLUSIONS 12

4 BIBLIOGRAPHY **14**

APPENDIX 1: Health Effects
APPENDIX 2: Measurement
APPENDIX 3: Information Sources

1 Introduction

Context

The Particle Measurement Programme (PMP) has been initiated primarily to ensure that future stages of European vehicle emissions regulations lead to the exploitation of the full potential of particulate emissions control technology. It is foreseen that this may be inhibited by the limits of detection of existing gravimetric filter techniques.

In parallel with the simple objective of achieving reductions in total PM_{10} mass emissions, there is the additional pressure to take account of metrics most directly linked to adverse health effects (which may include PM_{10}). However, it is recognised that long lead times to establish and quantify causal relationships in the health effects field will require this to be an iterative process. Thus, the PMP has had to make some assumptions, based on an assessment of current understanding across the many technical disciplines involved, in establishing its ‘core’ approach to meeting the objectives.

The ‘core’ approach is based on the assumption that the appropriate metric(s) will be applied, in the first instance, to the carbonaceous ultrafine component (accumulation mode) of the exhaust emissions. This mode appears to be robust and reproducible under measurement. The measurement procedure should ideally be compatible with existing type approval facilities and procedures. The measurement system should ideally also be easily adapted to respond to reprioritisation of appropriate metrics as evidence on health effects is quantified. In this context it is noted that nucleation mode particles continue to be researched and their measurement may have to be addressed in greater depth as more information on their potential health impact and/or reproducible measurement becomes available.

Methodology adopted

This review activity was aimed at monitoring the evolving understanding in those research fields which bear on the objectives of the PMP. The approach has been to assess the state of understanding at the start of Phase 1 and then monitor the reported output of studies which might add to this understanding.

The initial position was based mainly on the consolidation of the output of recent reviews – notably those listed in Table 1.1.

Table 1.1: Existing recent reviews

Date	Project source	Relevant aspects covered
February 2000	DG III: Vehicle Particulate Emissions Study	Health effects; regulated measurements; sampling; measurement instrumentation; project initiatives.
July 2000	US Environmental Protection Agency EPA/600/8-90/057E	Health effects.
February 2001	DETR contribution to PMP project definition	Health effects; measurement procedures; emissions control technology; project initiatives.
March 2001	DG TrEn: 'PARTICULATES' Project WP200 deliverables	Air quality; health effects; particle formation; sampling/dilution; measurement instrumentation.
April 2001	Swiss contribution to PMP Report PMP-CH1	Health effects; emissions measurement; emissions control technology.

This understanding has then been updated on the basis of additional information becoming available over the reporting period of this contract – essentially the period August – November 2001. The most prolific source of information over this short period has been the various conferences and meetings dealing with one or more of the relevant topic areas. These have included:

- 5th Nanoparticle Measurement Conference, Zurich, August
- PMP Experts Workshop, London, August
- European Aerosol Conference, Leipzig, September
- Inhaled Particles IX, Cambridge, September
- American AAAR Aerosol Conference, Portland, October
- Health Effects of Vehicle Emissions, Birmingham, November.

Much of the output of these meetings was not published in written form at the time that it was incorporated into this report. Other sources drawn upon have included websites, publications and personal communications.

Structure of report

In this report our understanding of the status of two key topic areas:

- health effects
- measurement

is summarised in Sections 2 and 3 respectively.

These summaries are based on the starting point of the distillation of the recent reviews, modified as appropriate by new information emerging within the period of this study.

Three appendices provide additional background detail in support of the main status summaries. Appendix 1 summarises the state of knowledge on the relationships between health effects and exposure to inhalable particles. Appendix 2 describes particle measurement techniques and sampling issues relevant to particle vehicle emissions characterisation. Appendix 3 is a guide to information sources on regulated emissions standards, health effects and particulate measurement. These appendices are essentially updated versions of recent reviews, including those for DG III and DG TrEn listed in Table 1.1, undertaken by the author.

2 Health Effects

Concern over particle-related health effects has stimulated the requirement for more detailed measurement of particle size, composition and concentration of the combustion-derived particle emissions to ambient air.

There are two types of study that can provide information on health effects of ambient particles:
- Epidemiology – acute and chronic exposure
- Toxicology.

Recent progress in these areas is dealt with in turn in the following sub-sections. New evidence on susceptible populations is included in the 'Epidemiology' sub-section.

This review follows on from the literature survey of Andersson & Rohe, produced for the UK DTLR in 2001. The health effects chapter of that review outlines the priority research areas identified by the US National Research Council in 1998 (NRC, 1998). Progress in the US against each of the priority areas identified has been further reviewed in the 3rd report of the National Research Council (NRC, 2001) with individual programme information available from the 5 US Particle Research Centers (see Appendix 3).

Details of European programmes may be found through the AIRNET web site (see Appendix 3).

In this section, new evidence arising during the reporting period is referred to specifically in the text and tabulated in the fourth column of Table 2.1. The quoted references are listed in Section 4. Those with publication dates after the reporting period relate to work which was accessed via conferences, projects or private communication, but not formally published until this report was already drafted.

2.1 EPIDEMIOLOGY

Population studies fall into two principal categories; short-term time series studies and long-term cohort based longitudinal studies. In each case, health effects have been related to mass based particle metrics (PM_{10}, $PM_{2.5}$), as these parameters are most commonly measured in ambient monitoring networks. There are, however, some limited data on health effects related to alternate markers such as particle number or surface area equivalents. In addition, a number of studies have been conducted on occupational exposure to diesel soot, although exposures are often poorly defined.

The short-term time series studies look at the association of health outcomes on a day by day basis versus a variety of air pollution markers (and other environmental measurements such as temperature, weather etc.). In these studies, whole population statistics are evaluated.

Most significantly, a number of key epidemiological studies have reported since the last UK PMP review (Andersson & Rohe, 2001). A recent re-analysis of time series studies

(NMMAPS; National Mortality and Morbidity Air Pollution Study) by the Health Effects Institute (Krewski *et al*, 2000) has supported the previous conclusions that acute particle exposure increases cardiac and respiratory morbidity and mortality. They also confirm the belief that key effect modifiers (most notably NO_2 and temperature) have been adequately controlled. Similar conclusions have been drawn from European data in the APHEA2 study. In addition, the strength of the effect of particle exposure on cardiovascular mortality in pollution episodes has been remarkably consistent across many developed and developing cities. These data continue to support a causal association between particles and health, on the basis of mass-based particle markers.

Longer-term cohort based longitudinal studies follow health outcomes in known populations within various cities, but with limited exposure data (usually annual-averaged PM_{10} or $PM_{2.5}$ data). Again, the Health Effects Institute has reported new data from the 6 Cities study and the American Cancer Society cohort studies (at 151 centres) and confirmed the finding that life expectancy is reduced in cities with higher air pollution. These data have been re-analysed by the UK Committee on the Medical Effects of Air Pollutants (UK COMEAP, 2001) which has calculated potential population life expectancy benefits from reductions in particulate air pollution. They conclude that it is more likely than not that there is a causal relationship between particulate air pollution and long-term health effects, and that the magnitude of the long-term health effects is at least equivalent to that of short-term effects, but may be up to ten times more significant.

Another recent study by Pope *et al,* 2002 using the American Cancer society cohort has found associations between lung cancer, cardio –pulmonary mortality and long-term exposure to fine particulate air pollution.

Thus, these data reinforce the existing health concerns against which improvements in air quality and reductions in emissions are being sought. Future insights are likely to be gained from improved source apportionment of ambient particles, for which methods exist, being adopted in epidemiology studies. Existing particle metrics are considered with respect to epidemiological evidence and summarised in Table 2.1.

Lung cancer risk has been evaluated for occupational exposure to diesel particulate. The most studied population has been US railroad workers initially reported by Garschick *et al*, 1988. Mortality data have been updated (from 1976 to 1996) and re-analysed. An increased incidence of lung cancer is observed in the population (Dawson & Alexeef, 2001; Garschick *et al*, 2000) but unit risk cannot be evaluated due to a lack of exposure data.

There have been a number of publications investigating health effects in specific population sub-groups.

New-born infants

The influence of air pollution on pregnancy outcome and birth-weight have been investigated with preliminary evidence that some components of air pollution including particles may be associated with low birth-weight (e.g. Bobak, 2000). Although these publications are less recent, they have typically not been cited in this context to date.

Children

Brunnekreef and co-workers (Janssen *et al*, 2001) have demonstrated an association between exposure to traffic and decreased lung function in children. Recent work in the Southern California Children's Health Study (Peters *et al,* 1999) has indicated that PM and NO_2 exposure (from all sources) may be associated with slower lung growth.

Elderly and diseased
A number of studies have addressed morbidity and mortality in the elderly and those already suffering from disease. Mortality studies in pre-existing cardiac disease suggest that air pollution may be associated (Checkoway *et al*, 2001; Goldberg *et al*, 2000). Salvi *et al*, 1999 and Sandstrom *et al*, 2001 have conducted human exposure studies with diesel particles, with only minor observed effects in atopic asthmatics and healthy subjects. An inflammatory response was observed at high exposure levels under light exercise.

2.2 TOXICOLOGY

Toxicology studies comprise both animal and human exposure studies to various particle mixtures. Table 2.1 summarises briefly the various particle metrics (size and composition) considered with respect to health effects, confirming the complexity of the problem of attributing risk from the particle mixture. There are insufficient data to fully prioritise metrics at this time, but some general conclusions can be drawn.

- Particle mass will continue to be an important metric, due to existing associations between mass measurements and health effects.
- Particle size distribution measurements will yield significant secondary information with respect to particle number, surface area and mass relationships and should remain a priority.
- Current hypotheses from toxicology studies suggest that ultrafine particles and metals may be important for acute inflammatory effects through an oxidative stress mechanism.
- The roles of other chemical components of the particle are less well understood. However, as chronic health effects increase in importance, further detail will be required for insoluble materials with their increased scope for long residence times in the body.
- Elemental carbon (EC) has been identified as having long-term effects on health and occupational exposure controls already exist.

Table 2.1 : Summary of particle metrics

Metric	Evidence source	Strength of evidence	New evidence in contract period or key publications
Particle mass	Epidemiology	Consistent association between PMx and reported health effects - a useful unifying PM measure.	HEI, 2000 Pope *et al*, 2002 COMEAP, 2001
Particle Size	Epidemiology Dosimetry Toxicology	Indications from epidemiology and toxicology that fine $PM_{2.5}$ is more potent than coarse PM on a mass concentration basis (although ambient composition will vary). Finer particles penetrate more readily into lungs, cells and through tissue barriers.	Pope *et al*, 2002 Wichmann *et al*, 2000
Particle Surface Area	Toxicology	Finer particles have greater surface area per unit of mass; A number of authors have demonstrated that toxicity for a material is consistent with available surface area, but that different materials have different relative toxicities.	Oberdorster, 2000
Ultrafine PM	Epidemiology Dosimetry Toxicology	Growing recent epidemiological database suggesting that this fraction may be of importance. Toxicology – inflammatory response on ultrafine exposure. Particle number concentration is also a metric of interest.	Wichmann *et al*, 2000 Lippmann *et al*, 2000
Metals	Toxicology	Have cytotoxic and inflammatory properties. The "metals hypothesis" is associated with the soluble metal fraction of ROFA and may be related to the ability of these metals to catalyse production of free radicals in tissues. Limited epidemiology data from Utah steel works study.	Ghio *et al*, EPA, NHEERL Donaldson *et al*, Edinburgh Dreher *et al*, EPA NHEERL Jaspers *et al*, EPA/NHEERL (all on-going studies not yet published)
Acids	Toxicology	Human effects observed in laboratory but significant neutralising capacity in lung.	Lippmann *et al*, 2000

Metric	Evidence source	Strength of evidence	New evidence in contract period or key publications
Organics	Toxicology	Compound-specific effects – particular concern for carcinogenic effects.	None
Sulphate / Nitrate	Toxicology	Human effects observed in laboratory; metric is often under-reported in ambient measurements.	Laskin, HEI (on-going studies not yet published)
Peroxides	Toxicology	Plausible toxicology route but ambient concentration is low.	Ghio *et al*, EPA, NHEERL Laskin, HEI (on-going studies not yet published)
Elemental Carbon and Soot	Epidemiology Toxicology	Soot has irritant, mutagenic, and carcinogenic properties that vary with delivered dose and the properties of the sorbed materials. Soot exerts both short-term (irritant) and long-term (carcinogenic) effects.	Vincent *et al*, 2001
Gaseous Co-factors (O_3, SO_2, CO, NO_2) (NO_2 also as effect modifier)	Epidemiology	Significant differences in health markers for different gaseous co-pollutants with location. Re-analysis of time series studies suggests that these have minor role relative to particles.	Kobzik *et al*, 2001

3 Measurement

In this field, much of the relevant understanding is emerging from major ongoing collaborative research project initiatives such as the PMP itself, the EC 'PARTICULATES' project and the CRC activities in the USA. Thus, although a few specific recent publications are referred to in this section, this review draws heavily on the understanding emerging from these project initiatives.

3.1 PARTICLE COMPONENTS

Particles emitted from vehicles have been discriminated into sub-groups, which can be addressed separately. These comprise:

(i) solid particles – this represents the accumulation mode comprising carbon, ash and metals, with prospective definitions based on sampling temperatures or the presence of such particles post-thermodenuder;

(ii) volatile particles – representing the nucleation mode, comprising both a sulphur-based component and a hydrocarbon based component;

(iii) specific composition components such as elemental carbon (EC), organic carbon, metals and others.

It is recognised that the solid particles in (i) are more fully understood and that this mode appears to be reproducible under various sampling regimes, such that it is suitable for accurate and precise measurement. As such, this mode represents the current focus of the GRPE Particle Measurement Programme (PMP).

However, it is also possible that future USEPA legislation (2007) might choose to regulate both solid and volatile particles. There remain problems with characterisation of the volatile nucleation mode particles. Whilst the mode can be reproduced for a fixed test regime for an engine on a day to day basis, the mode remains sensitive to environmental variables and technology and fuel differences. The measurement of 'nanoparticle formation potential' has been put forward as a means of assessing this mode and the EU 5th Framework 'PARTICULATES' programme is assessing reproducible means of producing this mode. However, it is noted that levels of nucleation mode particles generated under test are often less than those measured in roadway chase studies (Kittelson, 2001). Thus an intermediate approach may be required in the short-term, where 'nanoparticle formation potential' is modelled from measured levels of the particle precursors (sulphate and hydrocarbons), measured levels of accumulation mode solid particles (which will influence accumulation versus homogenous nucleation) and environmental conditions (temperature, relative humidity).

National legislation in the EU may focus on EC. In Germany, for example, there is existing occupational exposure legislation for EC. In this case it should be noted that regenerative trap technologies will selectively remove EC and may change the nature of solid particles, suggesting the need for other complementary measurement techniques.

It has been suggested (Wyser, 2001) that there is scope to consider particle mixtures as toxic equivalents as is currently the case with PAHs and dioxins. Thus, all metrics could be considered by weighting the measured concentrations by toxicity and adding the resulting products together. It is likely that such measurements may become more relevant and refined as the relative toxicity of each mode is better understood.

Emissions data from the laboratory have given information on the composition of nucleation and accumulation mode particles.

However, whereas field data have shown the presence of nucleation mode particles by roadways, their composition has been unknown. The most relevant field data derive from the work of the US Co-ordinating Research Council (CRC) programme (co-ordinated by David Kittelson). During 2001, data have been reported for composition of nucleation mode particles, supporting the hypothesis that these comprise a volatile sulphate core component (up to 5% by volume), and condensed hydrocarbons (Kittelson *et al*, 2001). A CRC project collaborator, Paul Ziemann of University of California, Riverside, has conducted thermal desorption-mass spectrometric analyses of diesel emission nucleation mode, confirming the presence of both sulphate and hydrocarbon species (Ziemann *et al*, 2001). Analysis of the hydrocarbon profile of the roadway nucleation mode suggests that these are a heavy fraction and are consistent with a lubricating oil source, rather than a fuel source.

3.2 PARTICLE METRICS

For solid particles in the presence of an effective thermodenuder, particle number and surface area will fully define the particle distribution, although direct measurement of particle size distributions may be of benefit as a crosscheck. Particle number and surface area may offer scope as core metrics as they offer high sensitivity with existing real-time measurement methods. Table 3.1 shows various measurements for a Euro III compliant diesel car relative to existing limits of detection (LoDs) for various techniques (Kasper, 2001). An early focus on particle number and surface area measurements does not preclude mass metrics, should new real-time techniques offer sufficient sensitivity.

Table 3.1: Existing sensitivity relative to Euro III emission levels

Technique	Metric	Sample period (s)	'Sensitivity' factor (Euro III/LoD)
Regulated filter	Mass	240	4
Coulometry	EC	240	3.6
SMPS	Number	90	9 000
Diffusion	Active	1.5	26 000

charger	surface		
Photoelectric	EC	1.5	7 000

As noted previously, appropriate metrics for volatile particles may require further research work, as existing formation methods cannot be fully correlated with the generation of such particles in roadway measurements, and they are prone to influence by environmental variables such as temperature, relative humidity and mixing efficiency. Thus, it may be more relevant at this time to conduct precursor measurements of sulphate, hydrocarbons and solid surface area, and develop models to determine the ‘nanoparticle formation potential’.

Chemical composition methods for elemental carbon are noted for their potentially high sensitivity and specificity but there are concerns that they might not fully represent future solid particle modes if, for example, organo-metallic additives become more prevalent.

Improved definition of metrics is key to driving instrument development for type approval with respect to instrument cost, maintenance and performance criteria.

3.3 SAMPLING

A focus on measurement of solid non-volatile particles with sampling at elevated temperatures will allow much greater flexibility for various sampling regimes. A number of sampling options exist, as discussed at the 5th Nanoparticle Workshop, Zurich 2001, as follows.

(i) Continued use of CVS systems although thermophoretic losses and transfer line and tunnel ‘memory’ effects might be significant. Thus separate tunnels might be required for ‘diesel and trap’, diesel and gasoline.

(ii) Direct sampling from tailpipe. This allows better control of the sample with respect to temperature and humidity (although these are less significant for the solid mode), dilution parameters and clean diluting air. However, tailpipe sampling will require accurate flow measurement under transient conditions (flow measurement and particle measurement method will require similar temporal resolution). It is recognised that there are new flow measurement methods under development and these will need to be validated in this context. It is possible, however, that information on fuel consumption, air intake and λ might be sufficient to characterise exhaust flow.

(iii) A third method involving introduction of dilution air at the tailpipe under conditions chosen to suppress nucleation and minimise thermophoretic losses.

A focus on solid particles in the accumulation mode is reinforced by the role of temperature and relative humidity being less significant in the formation of this mode than is the case for the nucleation mode particles (assuming the use of high temperature sampling with or without thermodenuder systems). It is notable that early measurements of Euro IV-compliant systems suggest that measured particle levels may be lower than ambient background particle concentrations. Thus, consideration is required as to whether diluting air should be pre-filtered. This would be relatively simple for tailpipe sampling and tailpipe dilution. Pre-filtering total make-up air for a CVS tunnel may be more difficult but is considered feasible.

An assessment of sampling techniques has been carried out in the aerosol laboratory and on drive cycle emissions and these data are reported in detail in a complementary research report (Dickens *et al*, 2002).

Background information on sampling issues and potential for system losses are included in greater detail in Appendix 2. The principal loss mechanisms are listed below.

- Inertial deposition (including gravity) – this is less significant for sub-micron particles. Losses are minimised by avoiding the use of sharp bends in the sampling apparatus (inertia) and avoiding long horizontal sections of pipe (gravitational settling).
- Diffusion – avoided by maintaining reasonable flow through the system and avoiding long residence times.
- Electrostatic deposition – avoided by the use of electrically conductive sample lines e.g. metal rather than plastics.
- Thermophoretic deposition – driven by temperature gradients and avoided by the use of heated sample lines.

3.4 TEST CYCLES

Transient test cycles are the most appropriate for the assessment of particle and gaseous emissions. However, consideration should be given to preconditioning cycles to minimise tailpipe memory effects, although current preconditioning might remain the most appropriate.

There is a need to incorporate measurement of emissions from regeneration cycles, including changes in gaseous outputs, such that measurements of continuous and periodic regeneration are treated on a similar basis.

It was noted that this issue is already being addressed separately via a proposed type approval trap regeneration test through the DEXA programme (Konstandopoulous, 2001) and also through separate proposals to GRPE for periodically regenerating systems (Lemaire, 2001).

3.5 INSTRUMENT SELECTION CRITERIA

An instrument evaluation matrix has been prepared (PMP-CH1) as an initial approach to instrument screening, and adopted as a preliminary template. A number of general points can be made as follows.

(i) The sensitivity of any adopted measurement method should be of the order of 10% of the adopted standard concentration for legislative purposes.

(ii) Sensitivity for current methods is such that particle number concentration and active surface area are likely to have sufficient sensitivity (e.g. Condensation Particle Counter (count mode), Diffusion Charger).

(iii) Complementary techniques may be required to verify size distribution in separate steady-state measurements or in real-time (e.g. multi-mobility analyser techniques).

(iv) Mass measurements are not precluded by this approach but improvements in sensitivity are required over existing gravimetric methods (e.g. Quartz Crystal Microbalance, optical methods).

(v) Elemental carbon-based methods may not be wholly appropriate where the carbon mode is reduced significantly by aftertreatment and the solid mode is predominantly composed of other species.
(vi) Solid mode particles, whilst a useful focus for diesel emissions measurement, may not be an appropriate measure for other combustion processes.

The participants in the PMP programme are testing a number of existing and development instruments, and current data are included in various test reports. Background information on established measurement techniques are included in greater detail in Appendix 2.

3.6 CALIBRATION

An important part of the sampling and measurement process will be the scope to calibrate chosen instrumentation, preferably *in situ*. Table 3.2 notes a series of relevant metrics and existing capability for traceable calibration.

Table 3.2: Calibration needs

Metric	Status
Particle size	Methods & materials available
Mass	Methods & materials available
Number	Methods available – traceability issues outstanding
Active surface	Methods available but untested in this context
EC	Methods available – traceability issues outstanding
Instrument flow	Volumetric methods available; must be aware of volumetric versus mass flow issues
Exhaust flow	Requires further investigation– traceability issues outstanding
Temperature	Methods available
Relative humidity	Methods available

A recent intercomparison exercise for mobility particle sizers has been conducted in Germany and Switzerland using diesel generators and a controlled propane diffusion flame to generate carbon particles (Dahmann *et al*, 2001). Measurements were conducted by participants using existing protocols from each laboratory prior to moving to a standardised protocol considering standardisation of techniques, software and hardware. The coefficient of variation for particle size and concentration was reduced to approximately 10% on standardisation.

3.7 CONCLUSIONS

- Immediate regulatory focus is on solid particles, which have proven to be robust under many sampling regimes. This simplifies sampling issues, thereby allowing a wider range of sampling options to be considered.
- Further research on volatile particles and their precursors is required before their significance in the context of future emission reductions for diesels and other combustion sources can be assessed.
- The solid particle mode can be isolated (and nucleation mode suppressed) by the use of high dilution and/or thermodenuders.

- Particle number and active surface area can be measured to high sensitivity with existing methods.
- Some mass measurement techniques under development may offer equivalent levels of sensitivity (for example, in the case of isolated nucleation mode emissions, mass can be derived from number and surface area measurements).
- Tailpipe sampling will require a measurement and calibration infrastructure for time-resolved volumetric flow.
- Existing test procedures might need to incorporate appropriate pre-conditioning to reduce tailpipe memory effects.
- Existing test procedures will need to take account of continuous and periodic trap regeneration.
- Sampling losses by impaction, diffusion, electrostatics and thermophoresis are well understood and have been minimised by the design of short, heated, electrically conductive sampling lines.
- There is an existing calibration standards capability for most of the key measurement parameters involved in the programme (particle size, mass, number, active surface, elemental carbon, volumetric flow, temperature, relative humidity) but a system for implementation on a systematic basis is not yet developed.

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