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Report of the

GRPE Particle Measurement Programme (PMP)

Government[1] Sponsored Work Programmes

July 2003.

[1] This summary report relates primarily to measurement programmes undertaken by France, Germany, Sweden, Switzerland and the United Kingdom, with additional contribution from Japan.

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0. Executive Summary

The Particle Measurement Programme (PMP) was established under the auspices of the UNECE/GRPE to develop a new system for measuring ultrafine particles emitted from heavy and light duty vehicles, which could replace or complement the existing particulate mass measurement system.

The main driver behind PMP is the impact of particles on human health. The PMP has no medical expertise and does not seek to pre-judge the advice that may emerge from medical experts with respect to the most crucial particle characteristics affecting human health. Nonetheless, given the body of medical opinion at this time, the PMP has moved forward on the basis of the precautionary principle.

This report provides an overview of government sponsored research from France, Germany, Sweden, Switzerland and the United Kingdom undertaken as part of PMP Phase II. The sponsoring Governments have agreed its contents jointly.

An important part of the first phase of PMP was the development of two draft testing protocols; one for light duty (LD) vehicles and the other for heavy duty (HD) engines. These standardised methodologies will contribute to the development of a robust test procedure that will reduce the variability of test results.

The government sponsored programmes have identified the following systems as having potential as candidate measurement systems:

- Modified 2007PM (A filter based method, incorporating certain elements of the measurement method proposed by the US EPA for heavy duty engines for implementation from 2007).
- Raw exhaust + thermodiluter + Electrical Diffusion Battery
- Constant Volume Sampler + Laser Induced Incandescence
- Raw exhaust + Laser Induced Incandescence
- Constant Volume Sampler + thermodiluter + Condensation Particle Counter
- Constant Volume Sampler + Photo Acoustic Soot Sensor
- Constant Volume Sampler + secondary dilution + MEXA (a filter-based method for determining PM mass with chemical analysis).

Most of these systems measure either total mass or the mass of elemental carbon, and therefore provide little additional information for regulatory purposes to the conventional filter mass approach. Improvements to the filter method, adopting some of the requirements in the US 2007 procedure for heavy duty engines, has shown improved repeatability at the low emission levels expected from future engines/vehicles. Whilst there remain some questions to be resolved, the results of the programme clearly show that improvements in mass measurement could be achieved by refinement to the filter based approach.

One of the measurement systems, CVS + thermodiluter + CPC, offers the advantage of counting the number of particles and so increases the overall sensitivity of the measurement procedure. Whilst not pre-judging the medical advice that may emerge, it appears prudent to further evaluate the potential of a number based system.

The repeatability of number based measurement systems is dependent upon volatile/nucleation mode particles, which can be present in very large numbers. A sample treatment system that removes these particles, or prevents them from forming, provides a more repeatable sample for measurement and is therefore an important element of the overall system. Such a treatment system must have the same impact on the sample presented to the CPC regardless of the engine, emission control system or fuel used

Within Phase II several national programmes have investigated the performance of commercially available and laboratory produced sample treatment systems. Both thermodenuding and thermodilution systems have been considered and the results to date suggest that the thermodiluter offers the best solution.

Therefore the two systems recommended for further consideration are:

- Mass - Modified 2007PM
- Number Count - CVS + thermodiluter + CPC

The draft test protocols used in this programme, and provided on the attached CD, should be further refined in the light of the experience gained. They should then form the basis of a proposal to amend the regulated procedures for measuring the emission of particles.

1. Introduction

1.1 Background

The Particle Measurement Programme (PMP) was established under the auspices of the United Nations Economic Commission for Europe's (UNECE) Group des Rapporteurs de Pollution et Energie (GRPE) to identify candidate systems for the measurement of ultrafine particles emitted from heavy and light duty vehicles. The aim is to develop a new measurement system that could replace or complement the existing particulate mass measurement system.

The mandate for PMP from GRPE includes:

- To develop regulatory test protocols, with instrumentation, to assess and control nano-particle emissions from (a) light-duty vehicles and from (b) heavy-duty engines within the range of 10 to 500 nm (the exact size range to be confirmed).
- The tests should be based on transient cycles and, if possible, conform to current regulated test cycles, i.e. European Light-duty and Heavy-duty (ETC) cycles, US Federal test cycles and also the World Heavy-duty Drive Cycle (WHDC).
- The protocol should focus only on the accurate assessment of carbonaceous particles within the measurement range indicated.
- To provide an assessment of current and advanced particulate control technology, as measured on the new protocol, to facilitate the development of new regulations aimed at further reductions in nano-particle emissions.

The aim of the programme is not to recommend specific measurement equipment but instead to specify performance parameters that will allow a range of manufacturers to produce suitable equipment capable of meeting the defined requirements.

A PMP Research Group was formed to assist in the development of the programme. It has provided a forum for interested parties to contribute their knowledge and to give those engaged in specific projects an opportunity to exchange views on their research.

Three PMP Researcher Group meetings were held during Phase I of the programme:

- London 31st July/1st August 2001
- Essen 29th/30th November 2001
- London 18th/19th March 2002

and these led to the construction of a comprehensive measurement system matrix and to the development of the test protocols that were used in Phase II.

Representatives of the following governments and stakeholders participated in one or more meetings:

- Governments:
  - France, Germany, Italy, Japan, the Netherlands, Sweden, Switzerland, United Kingdom
- European Commission
- Trade organisations:
  - AECC, CLEPA, CONCAWE, OICA,
- Research organisations /PMP contractors:
  - AEA Technology, EMPA, Institute of Toxicological and Aerosol Research at the Fraunkhofer Institute of Technology, MTC, Peter Brett Associates, Ricardo, RWTUV, Technical University of Munich, TTM, Stockholm University, University of Windisch, University of Biel
- Instrument manufacturers:
  - AVL, Cambustion, Dekati, ESYTEC Gmbh, Horiba and Matter Engineering

In addition, an informal meeting between the Swiss/German/UK researchers working on government sponsored programmes and the motor industry (ACEA), was held in Brussels on 20th June 2003. The aim of the meeting was to exchange information concerning the findings of the government sponsored programmes with respect to the differences observed between the current gravimetric (filter) based methods and the modified method as applied within the government sponsored work. This new approach is described later in this report.

1.2 Health impacts

The main driver behind PMP is the impact of particles on human health. The PMP has no expertise in health matters and this report does not seek to pre-judge the advice that may emerge from medical experts, however, the PMP has produced two summaries of the medical opinion available at the outset of Phase I. More recently the World Health Organization (WHO) Working Group report for the European Union's Clean Air for Europe (CAFÉ) Programme has been published (2003). This assesses the large body of research undertaken since the second edition of the WHO Air Quality Guidelines for Europe was agreed (published in 2000). It concludes that the fine particles ($PM_{2.5}$) are strongly associated with mortality and other health endpoints such as hospitalisation for cardiopulmonary disease. Several studies suggest that fine PM is more biologically active than coarse PM (particles in the size range 2.5 to 10µm), but other studies have found that coarse PM is also associated with adverse health effects.

A small number of studies have suggested an association between ultrafine particles (<100 nm) with symptoms in patients suffering from respiratory diseases. WHO have concluded, however, that more research is needed to establish the possible links between exposure to ultrafine particles and health impacts.

There remains therefore insufficient health information available to guide PMP on the specific size range of most interest for the protection of human health, and on the most crucial particle characteristics (e.g. number of particles or surface area). By investigating alternatives to the current mass based measurement system the PMP has operated under the precautionary principle, so as to be able to respond to political demand as and when it occurs.

1.3 This report

This report provides an overview of government sponsored research from France, Germany, Sweden, Switzerland and the United Kingdom undertaken as part of PMP. It focuses on the results of the second phase of the programme, as the results from the different laboratories are more comparable. The sponsoring Governments have agreed its contents jointly.

Individual work programmes have not been identified, nor discussed in detail, as the aim of this report is to provide a concise and coherent summary of the work undertaken. However work programmes from France, Germany, Japan, Sweden, Switzerland and the United Kingdom have all been taken into account in its preparation, and contributed to the conclusions and recommendations.

For those readers interested in more details of PMP and the Government research contributions, a CD has been provided to accompany this report containing full details of all the research summarised here, together with other PMP related papers. A list of the CD contents is given in Appendix A.

At the 45th GRPE Session the Organisation Internationale des Constructeurs d'Automobiles (OICA) tabled their contribution to PMP (Industry Comments on Proposed Particulate Measurement Techniques: Part 1 Synthesis Report). This report is available at www.oica.net (to find report follow WWH, then Particle Measurement Programme).

2. Methodology

2.1 Introduction

An important part of the first phase of PMP was the development of two draft testing protocols, one for light duty (LD) vehicles and the other for heavy-duty (HD) engines. These are based on existing regulatory procedures, and draw on the experience of several laboratories. These standardised methodologies will contribute to the development of a robust test procedure that will reduce the variability of test results.

The measurement of the number, size and surface area of nano-particles is more complex than the conventional measurement of particulate matter mass, as the result can change with experimental conditions such as temperature, dilution, and engine operating conditions. As there have been no standard measurement methodologies, comparison of results from different studies has, in the past, been difficult.

It should be noted that regulatory procedures for the measurement of emissions are inevitably a compromise between the use of a standard methodology to ensure good repeatability and reproducibility, and what happens in the real world. The current particulate matter mass measurement procedures, for example, influence the mass measured and if a different procedure were to be used the result would likely change. It is important that the procedures are broadly representative to ensure a fair test for the engine/vehicle whilst at the same time contributing towards the protection of the environment.

Sampling systems have an important influence on the particles, particularly when measuring numbers, and therefore within the work programmes the candidate measurement systems comprise both the sampling system and measurement device.

Any new measurement system must meet a range of criteria. Through the PMP Researcher Group and meetings between the individual contractors to the national programmes, the following criteria were identified as being most important for the assessment of potential measurement systems: repeatability, reproducibility, robustness, cost, and finally the traceability of the results.

- The term repeatability refers to the difference in results from a series of tests in the same laboratory with the same engine/vehicle, and is often expressed as the coefficient of variance (COV).

- Reproducibility refers to the results obtained from the same engine/vehicle measured using the same methodology at different laboratories.

- Robustness refers to how carefully a measurement system needs to be handled; i.e. it's suitability for a commercial testing environment rather than a specialist laboratory.

- Traceability refers to the ability to calibrate the system to a primary standard.

In addition to these criteria, it was agreed that the measurement system must have a detection limit sufficiently low to enable the measurement of particles at the level of emission from a current petrol engine or from a diesel engine equipped with a diesel particulate filter (DPF).

Although there may be factors that influence the particles measured, as long as all engines/vehicles are tested using a well defined test cycle, test procedure, fuel and sampling system the results should, in general, be comparable.

One of the most important factors for ensuring good repeatability for number counting is the suppression of the nucleation mode particles, typically comprising volatile compounds, formed by condensation during the dilution process. A number of factors can influence the formation of these particles, the sulphur content of the fuel or the dilution ratio for example, and these effects can vary with engine operation. It has also been suggested that 'false' measurements of nucleation mode particles can occur due to the pyrolysis of tube connectors or the re-entrainment of material previously deposited in the sampling system.

A number of sample conditioning devices to remove or suppress the formation of nucleation mode particles have been tested within the national programmes. These include thermodenuders and thermodiluters as well as early dilution and a 'diesel soot separator'. Not all instruments are compatible with all sample conditioning systems, and therefore not all combinations of conditioning systems and measurement instruments have been tested.

It is difficult to define concisely and accurately the composition of the resulting particles that are measured after the nucleation mode/volatile particles have been removed. The term 'solid' particle is often used. It should be noted that the particle measurement system used would, in effect, define the particles being measured.

In addition to evaluating new particle measurement devices, a modified version of the US 2007 gravimetric particulate measurement procedure for heavy-duty vehicles has also been evaluated within the national programmes.

2.2 Conditioning systems assessed

The following sampling systems were tested in Phase II:

Light duty

- Constant volume sampling (CVS)
- CVS + sample treatment (thermodenuder or thermodiluter)
- Rotary dilution
- Raw exhaust

Some of the measuring devices have their own dilution systems, which have been used after the CVS. In addition to the above sampling systems, a limited investigation of the potential of early dilution was undertaken.

Heavy duty

- Constant volume sampling (CVS)
- CVS + secondary dilution
- CVS + secondary dilution + sample treatment
- CVS + secondary dilution + tertiary dilution
- Raw exhaust
- Raw exhaust + hot dilution (rotating disk or double state ejector)

Any new measurement system should, ideally, be as compatible as possible with the existing regulatory test requirements in order to minimise the cost and time of homologation testing. Therefore, there was a presumption made at the start of the work that the current systems used for regulatory should be retained as far as is reasonable, practical, and consistent with the overall programme objective.

The dilution sampling systems were generally equipped with high efficiency particulate air (HEPA) filters to reduce the concentration of background particles in the dilution air.

Several sample treatment systems were tested:

- Thermodenuder – the sample is heated to desorb/evaporate the volatile compounds and an activated carbon/ceramic trap is used to absorb them. There are several different designs with the heating section and absorber section either in parallel or in series.
- Thermodiluter – a hot dilution system in which the formation of nucleation mode particles and the condensation of water within the diluter or sample line are prevented. Dilution is performed by a commercial rotating disk diluter, double stage ejector or porous diluter located adjacent to the exhaust system and prior to transport to the measurement devices.

The aim of the sample treatment is to remove or stop the formation of volatile particles whilst at the same time maximising the passage of the non-volatile particles through the device. To ensure good repeatability and reproducibility the parameters that affect these processes need to be understood and well characterised. If the losses are consistent then a correction factor could be applied to the results, to give the total number of particles. Therefore an integral part of the Phase II work was the development and application of a sample treatment characterisation methodology. The details of this are on the accompanying CD.

The following systems have been evaluated in PMP II:

- Commercially available thermodenuders from:
  - TSI
  - Dekati

- Laboratory thermodenuders from
  - Fraunkhofer Institute of Technology (Germany)
  - National Traffic Safety and Environment Laboratory (Japan)

- Hot dilution systems
  - Rotating disk produced by Matter Engineering
  - Ejector dilution systems by Dekati and Palas

In addition, one laboratory has explored the possible use of early dilution, close to the tailpipe, to prevent the formation of nucleation mode particles.

Finally the performance of a prototype diesel soot separator was evaluated. In this device the soot particles are charged using ultraviolet light and then removed by an electrical field. The field strength is sufficient to remove all charged particles, independent of their size, but the condensates/volatile particles are not charged and therefore remain unaffected. Therefore by sampling with and without the soot particle separator, the number concentration of 'solid' particles can be determined. The results from this work suggest that the carbon fraction in a post-DPF exhaust from one HD engine is between 76 to 80% over the ETC. For a LD diesel (post DPF) vehicle measured over the FTP the carbon fraction was 84%.

These assessments have been undertaken with a range of measurement devices using exhaust particles. In addition, laboratory tests using monodisperse aerosols of triacontane ($C_{30}H_{62}$), tetracontane ($C_{40}H_{82}$), eicosane, caesium iodide and sodium chloride have assessed the performance of the sample treatment systems. Results are presented as the penetration efficiency (percent), typically by mobility diameter.

2.3 Instruments assessed

Fifteen different types of instruments (some operate on similar principles) were included in the government sponsored programmes plus the gravimetric filter method, as shown below:

- Mass measurement systems:
  - Gravimetric (the European legislated/the modified US 2007 procedures)
  - Filter method with chemical analysis (measures mass of PM components)
  - Oscillating inertial microbalance (TEOM)

    - Laser induced incandescence (LII, measures mass of elemental carbon, and primary particle size)
    - Quartz crystal microbalance (QCM)
    - Photoacoustic absorption (PASS, measures mass of elemental carbon)
    - Coulometric (measures organic bound and elemental carbon)
    - Photoelectric charging (PAS, measures mass of elemental carbon)
    - Light extinction (opacity can be converted to mass)

- Number measurement systems:
    - Laser-light scattering (number and size distribution)
    - Differential mobility spectrometer (DMS, measures number and size distribution)
    - Optical counter (CPC, total number)
    - Electrical mobility/optical counter (SMPS = CPC + DMA measures number/size distribution)
    - Electrical Low Pressure Impactor (ELPI, number and size)
    - Diffusion battery (EDB, uses diffusion charging with a diffusion battery) (active surface, can be converted to number and size distribution)

- Other measurement systems:
    - Diffusion Charger (DC, active surface)

The aim of the various national programmes was to provide a comparative assessment when simultaneously exposed to a similar sample of particles from either an engine exhaust or an aerosol generator. At some laboratories the same sample conditioning system was used for more than one instrument; the disadvantage with this approach is that not all the instruments were presented with an optimum sample (for example the flow rate may not have been ideal). In one study the participating instrument manufacturers were permitted to sample either from the raw exhaust or from the full-flow CVS tunnel and could use their preferred sample conditioning system. The disadvantage of this approach is that the instruments were not presented with the same sample.

It should be noted that although several national programmes tested instruments with the same operating principle, not all the instruments tested were the same model. Different models can have varying sensitivities, response times etc. which can affect their performance.

2.4 Candidate systems tested

The candidate systems tested are shown in Table 1. In this table HD and LD indicates which measurement system (a combination of the measurement device, and sampling system and if appropriate sample treatment) have been used for testing HD engines and LD vehicles respectively. Some systems have been tested within more than one national programme.

Table 1: Potential candidate measurement systems tested in PMP II with heavy duty engines (HD) or light duty vehicles (LD)

Metric	Measuring device	Raw exhaust	Raw exhaust + other dilution	CVS	CVS + thermodenuder	CVS + secondary Dilution	CVS + 2nd dilution + thermodenuder/ thermodiluter	CVS + secondary Dilution + tertiary dilution
Mass	Filter methods			LD		HD		
	MEXA					HD		
	TEOM					HD		
	LII	LD/HD		LD/HD		HD		
	QCM							HD
	PASS			HD/LD		HD		
	MASS-Monitor		HD 2 stage ejector					
	Coulometric		HD partial flow dilution					
	PAS		LD/HD Rotary dilution	LD		HD		
	Opacimeter		HD Internal dilution					
	Laser-light scattering	HD	HD Rotary dilution					
Number	DMS			LD/HD		HD		
	CPC		HD 2 stage ejector		LD		HD	
	ELPI		HD 2 stage ejector					
	SMPS		HD 2 stage ejector		LD		HD	
Other	DC		LD/HD Rotary dilution					
	EDB		LD/HD Rotary dilution					
	Light extinction	HD	HD internal					

2.5 Draft test protocols

Draft PMP test protocols for LD vehicles and HD engines were derived to enhance the consistency of results within individual and separate programmes. These protocols were developed from the Researchers Meetings held during Phase I of the programme and were distributed for comment prior to use in Phase II. The protocols are based on existing European legislated procedures (UNECE Regulations 83, 49 and 24 and the corresponding EU Directives); a modified version of the US2007 testing methodology; and the draft procedures in ISO/DIS 16183. These protocols do not include raw exhaust sampling. Some of the key points of the protocols are set out below.

<u>Modified US 2007PM</u>

The full US2007 procedure has not been adopted due to the cost involved, particularly in respect to the standards it lays down for the clean room specification and the microbalance. This report therefore refers to the "modified US 2007PM" procedure.

The main departures from the standard European particulate mass measurement method in order to assess the modified US 2007 PM method are:

- Use of a cyclone pre-classifier in preference to the Chinese hat,
- Improved filtering of primary and secondary dilution air using a HEPA filter,
- Collection filter holder and cartridge assembly meeting US2007 specifications, with temperature closely controlled to a maximum of 52^{o}C and including a reduced size filter for HD,
- Improved specification for the collection filters,
- Removal of the secondary (back-up) collection filter.

The modified US 2007PM approach departed from the full US 2007 procedure in the following:

- Microgram balance with a precision of better than 2 μg for a clean filter; better than 0.25μg for a reference weight and a resolution or readability of 1μg,
- Differences in filter face velocities.

<u>Repeat tests</u>

For each of three drive cycles it was recommended that:

- At least seven tests be conducted contiguously in one single day,
- At least seven tests be conducted on different days,
- Any group of repeated cycles to follow the same warm-up and order of preceding tests as any other group of the same cycle.

<u>Light duty vehicles</u>

- The LD draft test protocol is based on existing regulatory procedures including using the NEDC/FTP driving cycles,
- Ideally the diesel vehicles tested should conform to Euro III for gaseous emissions and Euro IV particulate emissions; petrol vehicles should conform to either Euro III or Euro IV specifications; the vehicles should have been driven a minimum of 8000 km; and serviced according to manufacturers recommendations,
- Separate dilution tunnels should be used for petrol and diesel vehicles.

Heavy-duty Engines

- The HD draft test protocol is based on existing regulatory procedures, is specifically aimed at transient testing (including the World Heavy-duty Drive Cycle), but is also applicable to steady-state tests and to off-road applications with modifications.
- All HD engines should be equipped with DPFs, conform to both Euro III gaseous emissions and Euro IV particulate emissions requirements when a DPF is fitted.

Characterisation of Sample Treatment Devices

- The draft protocols suggest that sample treatment devices be characterised prior to inclusion in the evaluation of the candidate systems. The factors that influence performance should be measured and controlled to ensure repeatable performance.

Full PMP Draft Test Protocols

The full PMP draft test protocols are included on the CD supplied with this report.

Application of the Draft Test Protocols

These protocols were developed as the programmes matured and, due to the timing of individual programmes, not all the PMP studies used them. For example, the large multi instrument evaluation undertaken in close collaboration with the instrument manufacturers, whilst using many of the elements of the heavy duty protocol, used fewer repeat tests for the ESC cycle, and used the EPEFE engine conditioning protocols. It did, however, adopt the recommended modifications to the US 2007 mass measurement procedure.

Those laboratories that did use the protocols applied their own interpretation to the US 2007 test and therefore adopted some different approaches. For example, one laboratory undertaking heavy duty engine testing used heated dilution air for the secondary dilution system, controlled to 47°C (±5°C); and another laboratory used a heated filter holder with the temperature controlled to the same degree. Both these approaches are permissible under the US 2007 particulate matter measurement methodology. This may account for some of the differences in the results observed between the two laboratories in their comparisons of the current European filter method and the modified 2007PM method. Further development of the draft test protocols may be needed in order to remove the opportunity for interpretational differences.

2.6 Vehicle/engines and fuels

Seven LD vehicles and one HD engine were tested in Phase I, whilst nine LD vehicles and three HD engines were tested in the main Phase II national programmes. Of the LD vehicles seven were used in the evaluation of candidate measurement systems, and two in the evaluation of thermodenuders.

To enable an assessment of the measurement systems at different emission levels and chemical composition during the engine tests an adjustable bypass for the DPF was used in the HD studies. Tests were undertaken to simulate the emissions from an engine meeting the levels achievable by a DPF but using other PM emission control techniques. This was to ensure that any candidate measurement system is capable of measuring both low levels of carbonaceous and non-carbonaceous particles.

The engines/vehicles were tested with fuels that generally conformed to EU Directive 98/70/EC (2005) and had a maximum sulphur content of 10 ppm. The lubrication oil used was that as recommended by the individual engine manufacturers.

Table 2: Light-duty vehicles used in measurement system evaluation

Fuel	Engine type	After-treatment
Diesel	DI, Euro III	CRT with reagent
		DPF with active regeneration
		Oxy cat + additive based trap
		Oxy cat
Petrol	DI, Euro IV	TWC + EGR
		EGR+ TWC + NOx storage
		EGR+ Oxy cat + NOx storage

CRT = continuously regenerating trap; DPF= diesel particle filter; oxy cat = oxidation catalyst; TWC = three way catalyst; EGR = exhaust gas recirculation;

Table 3: Heavy-duty engines used in measurement system evaluation

Fuel	Engine	Type of DPF
Diesel	Euro III	CRT
		Catalyst based (CB-DPF)
		CRT

Table 4: Summary of the PMP II light-duty tests

Driving cycles used	Fuel Type	Fuel; Sulphur level
NEDC, FTP, plus steady states at 50 km/h, 80 km/h, 120 km/h and 140 km/h	Petrol	CECRF0299; S<1 ppm
	Diesel	CECRF0699; S = 2ppm
NEDC, FTP, steady states at 50 km/h, 80 km/h, and 100 km/h	Petrol	CECRF0299; S<1 ppm
	Diesel	CECRF0699; S = 2ppm

NEDC = New European Driving Cycle; FTP = US Federal test procedure;
Information on the lubricants used was not available. This table only covers the main PMP LD programmes (i.e. it excludes the separate thermodenuder/thermodiluter test programme). Note the diesel fuel used by 3 of the 4 laboratories came from the same batch.

Table 5: **Summary of PMP II heavy-duty tests**

Driving cycle used	Fuel; sulphur level	Lubricant; sulphur level
ESC, ETC, FTP, WHDC, SM, SCT	CECRF0699; S = 2ppm	
ESC, ETC, FTP, WHDC, SM	CECRF0699; S = 2ppm	5W/30;
ESC, ETC, SCT. SM	CECRF0699; S = 8ppm	10W/40; 3900ppm

ESC = European steady cycle; ETC = European transient cycle; FTP = US Federal test procedure; WHDC = World heavy-duty driving cycle; SM= single mode of a steady state test cycle; SCT = step change test (to determine instrument response time).
Note: The first two test programmes used the same batch of diesel fuel.

2.7 Instrument calibration

The ability to calibrate measurement systems to a traceable standard is very important. For mass-based methods the solution is already well established, whereas a primary standard for particle number and other metrics does not yet exist. Currently instruments that measure non-mass based parameters are calibrated against other instruments.

An aerosol generation system (Combustion Aerosol Standard - CAST) has been tested as a calibration device in several Phase II programmes. This generates sub-micron combustion particles that are similar to the particles emitted by diesel engines. The Swiss Federal Office of Metrology and Accreditation (METAS) has calibrated the concentration and size distribution of these particles.

Some national programmes have also used monodisperse aerosols to undertake daily calibration of the thermodenuders. For example a sodium chloride aerosol was sprayed into a reservoir and conducted through a differential mobility analyser (DMA) to provide particles of a defined size (mobility). The instruments requiring calibration were then connected to the output of the DMA.

2.8 Regulated gases

In most studies the regulated emissions were measured simultaneously with the particles.

2.9 Measurement system set-up

Figure 1 (Annex 4) shows schematic figures of the general arrangement for the measurement systems used in the programmes for engine and vehicle tests. Although there were some differences between the laboratories involved in the government-sponsored research, these figures provide a good indication of the general set-up used. Further details are provided in the main reports of the individual programmes.

2.10 Inter-laboratory comparison

The PMP has not attempted to evaluate the reproducibility of the candidate systems identified in this report. This was outside the scope of Phases I and II of the PMP. However, one national programme has investigated the reproducibility of a measurement system at four different laboratories, using three light duty vehicles: a common rail diesel with oxidation catalyst; a common rail diesel with DPF and oxidation catalyst and a conventional MPI petrol. This investigation used ELPI + CVS + thermodiluter as the measurement system but did not necessarily follow the PMP test protocols. The vehicles used are additional to those listed above in section 2.6.

3. Results

3.1 Introduction

The large number of measurement systems assessed within the national work programmes makes it difficult to summarise all the results succinctly. As the national programmes came to similar conclusions regarding the best performing measurement systems this report focuses on the results from these candidate systems:

<u>Mass based</u>

- Enhancements to the current gravimetric method (termed modified 2007PM in this report)
- Laser Induced Incandescence (LII)
- Photo acoustic soot sensor (PASS)
- MEXA (a filter bases method followed by chemical analysis)

Number based
- Condensation Particle Counter (CPC)
- Electrical Diffusion Battery (EDB)

A brief description of the measurement devices in these candidate systems is given in Annex 3.

Tests were undertaken using transient and steady test cycles, and single modes of steady test cycles. As PMP's mandate focuses on transient cycles this section of the report summarises the results of the regulatory transient tests only (i.e. FTP, NEDC, ETC).

The programme's main criteria for assessing the candidate systems were repeatability, reproducibility, robustness and traceability (see section 2.1). One of the primary functions of PMP Phase II was to investigate the repeatability within a single laboratory, and this summary focuses on this issue, and to a lesser extent, the robustness of the candidate systems. There is only limited data available within the government-sponsored PMP studies on reproducibility within different laboratories, and this is discussed in section 3.7. Traceability to a primary standard is discussed in Section 3.5 on calibration.

For full details of the results the reader is referred to the CD accompanying this report.

The programme is aimed at measuring particles at emissions levels below those required by regulation today, and most evaluation of the measuring systems has been undertaken using diesel vehicles/engines equipped with a DPF. These devices effectively remove the carbonaceous particles with a higher proportion of volatile exhaust aerosols being measured post-DPF. Due to the differences in exhaust composition, comparison between the measurement techniques is poor where the mass of elemental carbon is compared with total mass.

A number of terms have been used to describe the different types of particles emitted in vehicle exhaust. In this report 'particles' has been used to describe the exhaust particulate matter; it may comprise carbonaceous, organic carbon and/or sulphate components. Where a measuring system only measures one type of particle this is stated.

In general the sensitivity of number based measurement systems is much greater than mass based systems with respect to the concentrations post-DPF. The limits of detection (defined by the relevant ISO standard as three standard deviations) are dependent on measurement system set-up parameters such as dilution ratios.

Although several of the national programmes have used instruments with the same operational principles, different models have been used. Differences in sensitivity and response time can lead to different results between the programmes.

The emissions from the HD engines appear to be generally more stable during the tests than those from LD vehicles. This possibly reflects the differences between chassis and bench dynamometer testing, and approaches to HD and LD engine management.

All three LD vehicle technologies (petrol direct injection (PDI), diesel, and diesel plus DPF) tested were subject to variations in performance that were large compared with the anticipated repeatability (defined as the coefficient of variance = standard deviation/mean) of the measurement systems under investigation. That is, the poorer repeatability obtained reflects the greater variability in the emissions from LD vehicles compared to HD engines. However, the repeatability of the mass and particle number concentrations measured was often of the same order as those obtained for the gaseous emissions. For example in one programme repeatability was in the range 15% to 25% over the hot NEDC for CO; 13% to 21% for the same cycle for the modified 2007PM method and 13% to 37% for the conventional filter method.

3.2 Assessment of the enhanced gravimetric mass measurement method

Summary
The government sponsored PMP research has shown that gravimetric mass measurement methods, with suitable modifications, remain useful for regulatory purposes. Further work is, however, required to understand the crucial factors that influence the results and to improve the method for LD vehicles.

Robustness
The gravimetric measurement system is well established and proven to be robust.

Correlation with the other systems
The results of the studies comparing the modified 2007PM method with the current European filter method shows that it offers significant improvements in repeatability for HD engines, but more limited improvement for LD vehicles. The programme has identified some differences in the particle mass measured with the two methods, but further investigation would be needed to establish the reasons for this.

For some LD vehicles the repeatability was poorer with the modified 2007PM method than the conventional method. This is perhaps unsurprising given that the US 2007 PM method was developed for HD, not for LD. PMP has been pioneering the development of an improved methodology for the gravimetric measurement of mass for LD vehicles, and difficulties in applying a method developed for a different application can perhaps be expected.

In general, a rather poor correlation between the gravimetric methods and the other mass-based methods was observed for post-DPF exhaust. It is thought that very small, in most cases not reproducible, nucleation mode particles were detected by the gravimetric system. These are thought to be mainly hydrocarbon and sulphate particles produced in the DPF. This suggests that the chemistry of the fuel and/or lubricating oil will have a more significant effect on mass measurements in very low emission engines and vehicles.

However, when the DPF bypass was used to increase the carbonaceous fraction in the exhaust stream or a diesel vehicle without a DPF, the correlation was good, showing the influence of the particle chemistry on the results. Using CAST aerosols, which are carbonaceous, the correlation between the gravimetric methods and other instruments was also found to be good. In addition, good correlation was found between PM emissions measured using the gravimetric method and the LII from a LD diesel vehicle without a DPF.

Repeatability
The tests showed that the post-DPF samples had, in general, better repeatability with the modified 2007PM method than the non-DPF samples with the current PM method.

With the modified 2007PM method the close control and consistency of dilution air temperature enabled a large improvement in repeatability. In one HD study the repeatability did not appear to be related to the filter loading; the system was capable of repeatability below 10% on both daily and day-to-day bases, with post DPF filter loadings as low as 65 µg.

Using the heated filter holder approach also resulted in good repeatability over the WHTC; typically around 10% but less so over the ETC test (about 19%). In general in this study the repeatability decreased with lower emissions, even when using advanced gravimetric methods.

The repeatability with the modified 2007PM method was good over the NEDC (better than 8%) but poorer over the FTP (over 20%) for one DPF diesel car. This compares with a repeatability of 18% over the NEDC and 34% over the FTP using the standard PM method for the same vehicle.

Another study had an average (over 3 vehicles) repeatability of about 20% for the standard PM method over the NEDC and 16% for the modified 2007 PM method. For the DPF diesel vehicle over the NEDC a repeatability of 15% was found for the standard PM method, compared to around 10% with the modified 2007PM method. The petrol and diesel cars without DPF had poorer repeatability over the NEDC.

The repeatability of a measurement system can be very dependent on the inclusion of outlier results and on the closeness of the mean value to the limit of detection of the measurement system. For example, the elimination of an apparent outlier from the modified 2007PM data set for one DPF LD diesel vehicle improved the repeatability from 26% to 3.5% (with the hot FTP cycle). Thus there may be a case for removing outliers from the analysis but only where the vehicle characteristics can be shown to have changed during the testing programme e.g. when other emission measurements also exhibit significant change.

Time response
This system does not provide time-resolved results.

Limits of detection
The LD results suggests that the limits of detection of the modified 2007PM method may be about three times better than that for the conventional PM method.

Absolute measurements
The modified 2007PM method, using the heated dilution air typically gave lower emissions than the standard PM method. This is thought to be due to the standard method measuring a component that is not measured in the modified approach. This is likely to be the more volatile components of the PM, which are expected to pass through the filter at the higher temperatures used in the modified approach.

However, these results were not observed using the heated filter holder approach, with results being generally slightly higher with the modified 2007 PM method. Further work to understand these differences should result in a closer definition of crucial parameters.

Depending on the effects on measured values of any changes agreed in the future, correlation factors between the two methods may need to be developed.

3.3 Other mass measurement systems

Laser induced incandescence (LII)

Summary

Laser induced incandescence (LII) detects the enhanced thermal radiation (incandescence) emitted when carbonaceous particles are vaporised rapidly by a laser beam. It provides information on the mass of carbonaceous particles.

LII proved to be generally robust with good repeatability despite the emissions being close to the limit of detection for the diluted post-DPF samples. Repeatability was, however, poor for the PDI vehicles using NO_x storage as part of the emission control system. LII is less sensitive than number based systems, and has the disadvantage of being the most expensive of the commercially available measuring devices considered as having further potential. It might be a valuable, albeit expensive, tool for the detection of DPF failures and because of its transient capability, engine/aftertreatment development and in-service testing. The use of raw exhaust sampling would be advised to increase the instrument's sensitivity.

In summary it is unlikely that LII will have a role in testing compliance with regulations unless cost is reduced significantly as it does not offer significant benefits over cheaper carbonaceous measurement devices.

Robustness

The instrument performed well in three laboratory tests and needed no maintenance, while in another it had to be adjusted. In general the LII proved to be robust during the test programmes except in one study where the cell temperature exceeded 35^{o}C and the instrument automatically switched off.

Correlation with other systems

In general LII showed good correlation with most other measurement systems, except the gravimetric method (for example, the correlation coefficient was 0.95 for coulometry compared with 0.53 for the modified 2007PM method for a HD engine).

Repeatability

The HD data were generally very repeatable, even though post-DPF measurements were close to the instrument noise levels. The studies found that the post-DPF repeatability was in the range 4% to 14% over all ETC tests and 4% to 12% over the WTCHDC.

The repeatability for light duty vehicles was typically <10% but under some test conditions was significantly higher for the two PDI cars with an emission control system comprising EGR, TWC and NO_x storage. The effect of this technology on the variability in emissions from the vehicles would require further investigation.

Time response

The response of LII to concentration changes was fast and stable. It was able to detect individual peaks in particle concentration resulting from brief load peaks during the transient ETC test. The response time is strongly affected by the sample line length and dilution systems.

Limits of detection

The limit of detection measured in one HD test programme was about 22% of that measured post-DPF (0.037 ng/cm^3) on the ETC. In this test a diluted sample was measured; raw exhaust sampling increases the sensitivity. Additionally a more sensitive instrument is now available. Its sensitivity is, however, low compared to number based instruments.

<u>Photo acoustic soot sensor (PASS)</u>

Summary

The photo acoustic soot sensor (PASS) detects the sound pressure resulting from the expansion of the particles following absorption of a laser beam. It provides time-resolved carbonaceous mass data. The instrument proved to be robust, despite being a prototype, however its repeatability was inconsistent in the different government-sponsored PMP studies. Its sensitivity was slightly better than the LII, but is still poor compared with number-based systems.

In summary, PASS might be suitable for regulatory purposes, but further investigation of its repeatability would be needed.

Robustness

Its overall robustness during the testing programmes was good despite being a prototype. The system's electronics had to be adjusted during some of the tests, and advice on the appropriateness of this would be needed if PASS were used for regulatory purposes.

Correlation with other systems

The results correlated well with the results of many of the alternative measurement systems. Correlation with the modified 2007PM gravimetric method was poor. The correlation coefficients for the modified 2007PM were 0.51 and 0.53 in the two HD studies whereas for the coulometry method it was 0.95.

Repeatability

The PASS repeatability was not as good as some of the other instruments tested. In the HD tests the repeatability was 20 % or lower for transient tests depending on the test programme. In the light duty tests the repeatability was in the range 5 to 27%. The highest value was for a PDI vehicle.

Response time

The response time was similar to that for LII. The PASS was able to follow a transient test cycle and detect individual peaks in particle concentrations resulting from brief load changes during the ETC. The response time is strongly affected by the sample line length and dilution systems.

Limits of detection

The limit of detection measured in one programme was found to be approximately 38% of the emission measured from an engine equipped with DPF and assessed over the ETC test cycle (0.0294 ng/cm^3), i.e. similar to the LII.

MEXA

Summary
MEXA is a filter-based method with vaporisation of the particles followed by chemical analysis. It measures the mass of carbon, including the soluble organic fraction, sulphates, and total particulate matter averaged over the test cycle. It was robust during the measurement programme and there was good agreement with the gravimetric filter methods. In common with other mass based methods it is less sensitive compared with number based methods. It is an expensive instrument and is probably more suited to engine development than as part of a regulatory procedure. There are more limited data available for this instrument as it was only tested in one programme on one HD engine.

In summary, due to the cost of the equipment, the MEXA is unlikely to have a role to play in testing compliance with regulations.

Robustness
The filter sampling and its analysis by this instrument did not pose any problems during the one test programme that assessed this instrument.

Correlation with other systems
The MEXA results correlated well with those from the gravimetric method, with a correlation coefficient of 0.998. This was due to the instrument measuring the mass of components additional to the carbonaceous particles. The correlation with those methods measuring only carbonaceous particles was less good, for example the coefficient for the correlation with the coulometry method was 0.36.

Repeatability
This measurement device shows good repeatability, on a transient cycle, in the range 3% to 9% over the ETC post DPF.

Response time
This system does not provide time-resolved results.

Limits of detection
The limit of detection measured in one programme was about 18% of the measured ETC post-DPF concentration. In common with other mass based methods it is less sensitive compared with number based methods.
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3.4 Number measurement systems

Condensation Particle Counter (CPC)

Summary
The Condensation Particle Counter (CPC), also known as a Condensation Nucleus Counter (CNC), provides time-resolved total number concentrations by enlarging nanoparticles, followed by their optical detection. In count mode particles are detected singly. This requires a very dilute sample. In opacity mode the CPC detects all the particles within a volume of air and converts this to a particle concentration using a calibration function. The former mode is preferred as it is more accurate.

This instrument, when operated with suitable sample pre-treatment, has good repeatability over transient test cycles. This is typically better than the standard gravimetric method for HD engines. For LD the repeatability is poorer than for HD but is similar to that found for LD with the modified 2007PM method.

CPC is robust, sensitive and commercially available. It is medium priced, but this may drop as the technology matures and the demand increases. In summary, the CPC (with sample treatment) offers the best option for a number based measurement system.

Robustness
The overall robustness of the CPCs tested was generally good during the entire programme although there was one instrument failure. These instruments are commercially available and have been used extensively in laboratory testing programmes.

Correlation with other systems
A good correlation was found with a range of other measurement instruments except for the gravimetric method. For example, in one study without sample pre-treatment (e.g. a thermodenuder) the correlation coefficient between CPC number and gravimetric mass was 0.28, with a thermodenuder in another study it was 0.49 with HD engines. This compares with the correlation coefficients for PASS and LII, which were 0.986 and 0.885 respectively.

Repeatability
CPC with a thermodenuder can have excellent repeatability (3%) for HD tests carried out within a single day, although this was not found in all the laboratories. In one programme a CPC and thermodenuder were used with the same HD engine, in both Phase I and Phase II. Between the two programmes single day repeatability levels for ETC improved from 18.5% (Phase I) to 3.4% (Phase II). This can be attributed to closer control of the testing parameters in Phase II arising from the use of the draft PMP test protocol. Figure 4 (Annex 7) shows the repeatability over the ETC for the Phase II tests. Poorer day-to-day variability was found which is thought to be due to particles being introduced into the CVS through vents in the dilution system or via the exhaust system bypass.

For LD vehicles the repeatability for tests undertaken on a single day was poorer than for the HD engines. For example, for one DPF diesel vehicle it was 22% over a hot NECD. This poor repeatability for LD vehicles is similar to that found for other measurement methods and is likely to reflect the greater variability in emissions during the test procedure compared to a HD engine.

Response time
The time response of the CPC is dependent on the model used. The CPCs tested were able to follow a transient test cycle and to detect individual peaks in particle concentrations during brief load changes. However those instruments with a slower response time showed lower peak concentrations during the transient tests.

Limits of detection
CPCs have the greatest sensitivity of all the instruments tested. A detection limit of 60 particles/cm^3 was found with one model in one study, although higher detection limits were found with other models in other programmes.

System specification

If CPCs are to be considered further for regulatory purposes they need to be well defined to ensure good reproducibility of results across different laboratories. For example, CPCs with internal flow splitting or dilution, and using the opacity mode are not recommended. Instrument response time also affects the results.

The lower particle size limit varies from CPC to CPC, and this will need specifying. It may be that the particles of most interest in the regulatory context are those above, say, 30nm and that there is no added value in measuring smaller particles.

Because of the limited concentration range of many CPCs secondary and/or tertiary dilution systems may be required. Dilution systems are critical components of any candidate system and standard procedures for secondary/tertiary dilution should be established.

There is some evidence that particles may be entering the sample conditioning system though small vents, allowing air from the test cell to enter. Test cell air is dirtier than the dilution air, is unfiltered, and often has a high level of nucleation mode particles. This issue needs to be addressed to avoid different facilities measuring different levels depending on background values and CVS/dilution system design.

Electrical Diffusion Battery (EDB)

Summary

The Electrical Diffusion Battery (EDB) provides time resolved number concentrations, and active surface ($\mu m^2/cm^3$), including size information. Ions are attached to the particles, which are then attracted to electrically insulated screens. Smaller particles have a higher diffusivity and are removed earlier than larger particles. The device measures the current generated by the charged particles; the sum of all the currents represents the active surface of the particles. The number size distribution is calculated assuming a monomodal lognormal distribution. This type of distribution is unlikely post-DPF. It is expected that further developments will overcome this shortcoming. The EDB's main advantage is the ability to discriminate <50nm particles without the need for sample conditioning (i.e. a thermodenuder).

The results from the EDB correlate well with those from many of the other systems tested, except for the gravimetric method. It proved to be robust despite being a prototype. However it is considered to require further development before it can be used for regulatory purposes as there was poor repeatability when used with DPF diesel and PDI cars, and there were large differences in the repeatability for number, mobility and active surface area.

In summary, the EBD will require further development before it can be considered for use for testing compliance with regulations.

Robustness

The EDBs tested were prototypes, but proved to be very robust during the tests.

Correlation with other systems

Measurements post-DPF revealed differences in absolute number concentrations compared to other number measurement devices. However one HD study found a good correlation with the results from PASS, LII and CPC (when the idle result was excluded). The correlation coefficients were 0.95, 0.93 and 0.97 respectively. This compares with correlation coefficient of 0.48 for number and 0.51 for active surface compared with the gravimetric method.

The current algorithms assume a monomodal lognormal distribution of the measured aerosol, which is unlikely with post-DPF. It is expected that further development will overcome this shortcoming.

Repeatability
The instrument performed well with repeatability better than 15% at post-DPF levels for HD engines operating over the ETC and WHTC. With the DPF diesel and PDI cars the EDB performed poorly. There were large differences in the repeatability for number, mobility and active surface area, with values up to 66%.

Response time
The response time of the EDB to defined concentration changes was fast and stable. It was able to follow a transient test cycle, however, the detection of individual peaks in particle concentration resulting from brief load peaks during the transient ETC cycle was limited.

Limits of detection
The LOD was about 30% of the measured post-DPF concentrations in one study (16,700 particles/cm^3), which is significantly less sensitive than the CPC

Sample conditioning
The EDB's response is independent of both particle chemistry and density, and without some form of sample conditioning, this method cannot discriminate between solids and condensed particles.

3.5 Calibration

<u>Introduction</u>

Any measurement system used for regulatory purposes must be capable of robust calibration. The development of a calibration procedure was not explicitly included in the government sponsored PMP studies, and the manufacturers themselves 'calibrated' most of the measuring devices prior to the programme. However, calibration remains an important issue for the development of a regulatory test procedure.

This section of the report discusses some of the issues of calibration of measuring devices. It is important, however, to recognise that all the relevant parts of the measurement system must be calibrated according to current best practice. This includes, for example, the calibration of the flow meters to ensure that dilution ratios are accurately known.

Engine exhaust particles are heterogeneous, varying in size and chemical composition, making the development of a calibration procedure difficult.

There are several types of calibration. Routine calibration is undertaken in the laboratory at intervals defined by the stability of the system and using a standard reference material. Ideally this would use a similar material to that which the measuring device samples. The long-term stability of the particle instruments tested in PMP is not yet established. For regulatory purposes it will be essential to define this to establish calibration intervals

Between routine calibration intervals 'scan checks' are undertaken to ensure that the device is correctly responding e.g. zero, mid-range and full scale.

In addition, the standard reference material may need to be calibrated against a primary reference method. This typically would not be undertaken by the measurement laboratory, but would be undertaken in a specialist laboratory.

Gravimetric methods

The mass based candidate measurement systems (i.e. the gravimetric methods), which use a filter to collect the particles, can be calibrated by weighing reference weights on the microbalance. These reference weights have been calibrated against a primary standard traceable to national standards. This is a well-established procedure that has been undertaken by vehicle testing laboratories over a period of several decades.

Mass of carbonaceous particles

The candidate systems that measure the mass of the carbonaceous particles in engine exhaust can be calibrated using the coulometric reference method (VDI 2465). However, this procedure is time consuming and therefore its use is not to be recommended on a frequent basis. It might, however, be possible to develop an appropriate calibration procedure using this method if the measuring devices prove to be stable over long periods of time.

Chemical Speciation of particles

The chemical speciation of the particle components (i.e. MEXA) can be calibrated using traditional methods for the gas analysers.

Particle number concentration

The most difficult systems to calibrate are those based on the measurement of the number of particles. The calibration procedures for combined particle size and number measurements (i.e. number size distribution) are more complex than for particle number alone.

At present, neither a reasonably fast calibration method for routine use in the laboratory nor procedures traceable to a primary standard are available for either particle size and/or number, although proposals do exist for a straightforward number calibration.

In one government sponsored PMP study, for example, a CPC (measuring the number of particles one by one) was calibrated using a sodium chloride aerosol. This aerosol was formed by the dispersion of a 1% NaCl solution which was separated into different sizes using a differential mobility analyser (DMA). Each particle exiting the DMA carries at least one electrical charge. The charge distribution of these particles is known and the average charge per particle is measured. The corresponding current measured by the electrometer can be related to the counts measured by a CPC; and a correlation factor generated. By using an electrometer the calibration value is traceable (to voltage, amperage, and flow).

This and other similar approaches developed within the national PMP programmes may need to be developed if a number based test procedure is used for regulatory purposes.

Combustion Aerosol Standard (CAST)

Combustion Aerosol Standard (CAST) is a calibration system developed in Switzerland. This device uses the controlled combustion of propane followed by quenching with nitrogen gas to produce soot particles with a monomodal distribution.

A rotating disk diluter is used to achieve the appropriate concentration. The Swiss Metrology Institute (METAS) has certified CAST to a typical measurement uncertainty of ~5% and 20% to 30% for size and number concentration respectively.

The government sponsored PMP programmes show that CAST generated aerosols can have good repeatability when measured with a SMPS. This can be illustrated by the particle number concentration and particle size repeatability of 8% and 12% respectively across 13 test days measured in one study. This is more repeatable than the engine tests.

Another study has shown that CAST is stable with respect to the average size diameter but has a tendency to decrease the number of particles generated over time (27 tests). The larger (100nm) particles appear to decline at a faster rate than the smaller particles (30nm).

A third study has shown that the nominal size of the particles generated by CAST did not always agree well with the SMPS mobility. For example the nominally 55nm particles were an average of 84nm, the 80nm were 93nm, 110nm were 107nm and the 220nm particles were 165nm. In this study, however, the internal CAST dilution system was not used; instead the complete CAST flow was fed into the exhaust gas line, which normally connects the tailpipe to the CVS tunnel. This may have affected the size of particles produced.

Further work is required to determine the role of CAST in calibrating measuring devices.

3.6 Removal of volatile material by sample treatment

A number of studies have shown that it is necessary to remove volatile particles to ensure repeatable measurements when measuring particle number. Laboratory tests have shown that there are several sample treatment systems that can potentially do this:

- Thermodenuders
- Thermodiluters
- Early dilution

An important part of the national PMP research was investigation into the performance of the sample treatment devices to determine the removal of both the volatile and the non-volatile particles from the exhaust sample. This has been defined in the national programmes as the penetration (i.e. the percent of the sample particles that are detected upstream of the device). The lower the penetration the greater the losses in the sample treatment device, and the more inaccurate the results. The aim is for a poor penetration rate for volatile particles, and good penetration rate for the non-volatile particles

It is important to characterise the devices in terms of the losses. If these are consistent, and can be well defined, a correction factor can be determined to enable the results to be recalculated to yield the total number of non-volatile particles.

Thermodenuders

Thermodenuders heat the sample to desorb or evaporate the volatile compounds, which are then absorbed onto an activated carbon/ceramic trap. The evaluation of their performance has raised some issues regarding their suitability for use in regulatory tests.

Figure 3 (Annex 6) shows the effect of one commercially available thermodenuder on the number size distribution. There was good repeatability and significant losses of 20nm particles were observed.

The evaluation of thermodenuders has show that their performance can be very repeatable and that the performance of two matched thermodenuders is similar. They also can effectively remove large volatile (C30) particles. However, it has also raised the following issues:

- Entrainment of carbon from the thermodenuder bed with some thermodenuders
- Dependence on the chemical composition of the exhaust particles
- Relatively large losses of the non-volatile particles

Figure 2 (Annex 5) shows the particle composition for selected steady state operating conditions for a HD engine for engine out and post-DPF exhaust. The potential differences in aerosol chemistry from cycle to cycle could result in the thermodenuder performance over an ETC being different, for example, to that over a WHDC. Thus if they are to be used their performance will need to be characterised for the specific application for which they are being used.

In addition, if the exhaust chemistry varies from engine to engine owever, the
the performance of the thermodenuder may also differ with engine type. To use these devices would require each to be characterised specifically for the test cycle and engine for which it is being used, which is unlikely to be acceptable for regulatory testing.

Thermodiluters

Thermodiluters are a hot dilution system in which the formation of nucleation mode particles and the condensation of water within the diluter or sample line are prevented. These devices appear to offer more promise for regulatory testing than thermodenuders.

The best performing thermodiluters show virtually no loss of particles in any size range, and therefore these systems offer the potential advantage of not requiring any correction of test results. They are also not dependent on activated charcoal that requires periodic replacement, and can follow transient test cycles with little delay.

Two thermodiluters have been tested within the national PMP Phase II. The effect of one system on the number size distribution is shown in Figure 3 (Annex 6). Thermodiluters have been shown to effectively remove large volatile compounds (C30 and C40) by more than four orders of magnitude. These are heavier than those likely to be encountered in engine exhaust, and therefore as these volatile particles can be removed those present in engine exhaust should also be effectively removed. The hot dilution system using a heated commercial rotating disk diluter showed almost no loss of 20, 50 or 100nm CAST particles. This system also showed very good repeatability.

Early dilution
Controlling the primary dilution process can limit the formation of nucleation mode particles, thus replacing the need for a thermodenuder.

In PMP limited tests have been undertaken to assess the concept's feasibility within the regulatory context. Initial results suggest that it could reduce the number of particles from DPF diesel and PDI vehicles by about an order of magnitude, under the conditions tested. By contrast, the effect of early dilution on the diesel vehicle (without DPF) was to increase the number of nucleation mode particles. Taking account of the published literature and the result of the preliminary investigation it has been concluded that it would be difficult to exploit this concept for regulation unless major research effort is undertaken to quantify its potential. This is outside the scope of PMP.

3.7 Inter-laboratory comparison

Preliminary results of the initial inter-laboratory comparison for one vehicle (diesel without DPF) are shown in Figure 5 (Annex 8). The results for this one vehicle look promising; further data is due.

4. Conclusions

The government sponsored programmes have considered the following systems as having potential as candidate measurement systems:

- Modified 2007PM
- Raw exhaust + thermodiluter + EDB
- CVS + LII
- Raw exhaust + LII
- CVS + thermodiluter + CPC
- CVS + PASS
- CVS + secondary dilution + MEXA

Most of these systems measure either total mass or the mass of elemental carbon, and therefore, for regulatory purposes, provide little additional benefit to the conventional filter mass approach (other than time resolution). Improvements to the filter method, adopting some of the requirements in the US 2007 procedure for heavy duty engines, has shown improved repeatability at the low emission levels that may be expected for future emission standards. Whilst questions remain to be resolved on some details of the procedure, it is considered that refinement to the filter based approach will improve measurement accuracy using this metric.

One of the measurement systems, CVS + thermodiluter + CPC, offers the advantage of counting the number of particles and so increasing the overall sensitivity and scope of the measurement procedure. Whilst medical advice concerning the effect of different particulate measurement metrics on human health is yet to be given, it is considered prudent to further evaluate the potential of a number based system.

Number based measurement systems are sensitive to the volatile/nucleation mode particles, which can be present in very large numbers. A sample treatment system that removes these particles, or prevents them from forming, to ensure good repeatability and reproducibility, e.g. by only counting solid particles, is an important element of the overall measuring system. Such a system must have the same impact on the sample presented to the CPC regardless of the engine, emission control system or fuel used.

Within Phase II several national programmes have investigated the performance of commercially available and laboratory produced sample treatment systems. The results to date suggest that thermodilution offers the best solution.

5. Recommendations

Based on an overall judgement of their performance with the key criteria identified in section 1 and having regard to the results from the government sponsored PMP programmes, it is recommended that the following two systems be considered for future regulatory use:

- Modified 2007PM (a gravimetric filter based mass measurement system).
- CVS + thermodiluter + CPC (a number based measurement system).

ANNEX 1

PMP Government Sponsored Work Programmes – Cover CD Contents.

Background

EU Memorandum.
PMP Overview.
Terms of Reference.

Health Effects

Presentations:

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Interaction of nanoparticles with internal lung surfaces - what we can learn from experimental work with fine particles (Professor Gehr - Institute of Anatomy, University of Berne).
Health effects of ambient particles including diesel particles – Workshop on Diesel DPF, Tokyo March 2003 (Dr Ishihara – Tokyo Women's Medical University).

Reports:

Swiss Report, CH1 (Phase I).
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WHO Report.

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Report: meeting November 2001 – Essen.
System Matrices – ex. Essen.
Report: meeting March 2002 – London.

System assessment – Phase I

PMP Phase I GRPE Report.
Swiss Report CH2.
Swiss Report CH3.
UK Report – Heavy-duty.
UK Report – Light-duty.

System Assessment – Phase II

PMP Phase II GRPE Report.
German test programme (heavy-duty & light-duty). RWTÜV.
Swiss test programme (heavy-duty). EMPA.
United Kingdom test programme (heavy-duty). Ricardo.
United Kingdom tests programme (light-duty). AEAT.

Thermodenuder/Thermodiluter

Presentations:

Thermodenuder activities in Japan. (NTSEL).

Reports

Swedish test programme (MTC).
Swiss test programme (University of Applied Sciences, Windisch University).
Proposal for Thermodenuder Characterisation.

Glossary

2007PM	The new US method for measuring particulate mass from heavy duty engines, for implementation with the year 2007 standard.
ACEA	European association of motor manufacturers
AECC	European association of automobile catalyst manufacturers
Accumulation mode	Particles within a certain size distribution comprised of agglomerated primary carbon particles and condensed materials. Peak typically located above 50nm.
CAFE	Clean Air For Europe Programme of the European Commission
CAST	Combustion Aerosol Standard
CB-DPF	Catalyst Based Diesel Particulate Filter
CLEPA	European Association of Automotive Suppliers
CO	Carbon monoxide
CONCAWE	Conservation of Clean Air and Water in Europe – the oil companies' European organisation for environment, health and safety
COV	coefficient of variance = standard deviation/mean, expressed as a percentage; a measure of repeatability
CPC	Condensation Particle Counter (a proprietary Condensation Nucleus Counter, CNC)
CNC	Condensation Nucleus Counter
CRT	Catalytic Regenerating Trap
CVS	Constant Volume Sampler
DC	Diffusion Charger
DF	Dilution Factor
DI	Direct Injection
DIS	Draft international standard
DMA	Differential Mobility Analyser
DMS	Differential Mobility Spectrometer
DPF	Diesel Particulate Filter
EDB	Electrical Diffusion Battery
EC	Elemental carbon
EGR	Exhaust gas recirculation
EPLI	Electrical Low Pressure Impactor
EPEFE	European programme for engines, fuels and emissions; a joint oil and motor industry research programme undertaken in the mid 1990s.

ESC	European steady-state test cycle
ETC	European transient test cycle
EU	European Union
EUDC	Extra urban driving cycle
Euro "x"	Referring to European legislation for the control of emissions e.g. Euro III (implemented from 2000) and Euro IV (from 2005) for light duty vehicles and heavy-duty engines.
FTP	US Federal Test Procedure
PDI	Petrol Direct Injection
GRPE	UNECE Working party on Pollution and Energy
HEPA	High Efficiency Particulate Air
ID	Internal diameter
ISO	International Standards Organization
LD	Light duty vehicle
LII	Laser Induced Incandescence
LOD	Limit of detection
HD	Heavy duty engine
METAS	Swiss Federal Office of Metrology and Accreditation
MEXA	A filter-based method for determining PM mass with chemical analysis
MPI	Multi-point injection (for a petrol vehicle)
Modified 2007PM	A modification of the US 2007PM measurement methodology, as applied in PMP.
Nanoparticle	A particle of diameter <50nm
NEDC	New European Driving Cycle (i.e. the current European legislated light duty driving cycle)
nm	Nanometre $=10^{-9}$m.
NOx	Oxides of Nitrogen = nitrogen dioxide + nitric oxide
Nucleation Mode	Particles comprising either a small solid nucleus with condensed volatile materials or wholly comprised of condensed materials. Typically <50nm diameter
OC	Organic carbon
OICA	Organisation Internationale des Constructeurs d'Automobiles
Oxy-cat	Oxidation catalyst
Particle	Exhaust aerosol; solids, liquids and water as measured by the candidate system under evaluation
PAS	Photoelectric Aerosol Sensor
PASS	Photo acoustic soot sensor
PM	Particulate Matter (all materials collected by the conventional filter method)

$PM_{2.5}$	Particulate matter with an aerodynamic diameter of less than 2.5 microns
PM_{10}	Particulate matter with an aerodynamic diameter of less than 10 microns
PMP	Particle Measurement Programme
ppm	parts per million
QCM	Quartz Crystal Microbalance
Repeatability	The variability in test results with the same engine/vehicle measured in a single laboratory; defined as the coefficient of variance (see COV). Described in terms of good (low COV), moderate or poor repeatability (high COV)
Reproducibility	The variability on test results with the same engine/vehicle measured using the same methodology at different laboratories.
SCT	Step change test
SM	Single mode of a steady state test cycle
SMPS	Scanning Mobility Particle Sizer
TD	Thermodesorber
TEOM	Tapered Element Oscillating Microbalance
ULSD	Ultra Low Sulphur Diesel Fuel (by definition <50ppm S)
Ultrafine particle	A particle having a diameter greater than 50nm but less than 100nm.
UNECE	United Nations Economic Commission for Europe
VDI	Verein Deutscher Ingenieure
WHDC	World Heavy-duty Drive Cycle
WHSC	World Heavy-duty Steady Cycle
WHTC	World Heavy-duty Transient Cycle
WHO	World Health Organization

ANNEX 3

Short descriptions of the particle measurement instruments included in the candidate systems

Laser-induced incandescence soot analyser (LII)
Soot particles are rapidly heated to their vaporisation temperature within the probe. This is achieved by means of a highly energetic laser pulse. The enhanced thermal radiation generated is then detected. The mechanisms involved are; absorption of the laser energy, change of internal energy and the different heat loss mechanisms; vaporisation, heat conduction to the surrounding gas and thermal radiation - which is the measurement signal.

The signal maximum provides soot mass concentration, and the signal decay yields specific surface area or primary particle size. To determine absolute concentrations, calibration with a carbonaceous aerosol generator and comparisons with coulometric measurements are required in advance. There is an excellent linear correlation between the LII signal and coulometry which verifies the EC specificity. To determine the primary particle size, it is necessary to measure the ambient exhaust temperature since some tens of nanoseconds after the laser pulse, the heat conduction is the dominant heat loss mechanism. Consequently, the temperature gradient between the particles and the surrounding gas is an important feature for inclusion in calculations.

LII enables the possibility of online and in-situ determination with high temporal resolution up to 20 Hz allowing investigations of highly dynamic and transient behaviour. The main benefits of this system are, besides its high sensitivity which is quoted as lower than 5µg/m^3, the flexible applicability to raw exhaust gas flow without any dilution, conditioning and sampling as well as to CVS- and partial flow systems.

PASS
Absorption of a modulated infrared laser beam by the carbon particles leads to modulating heating and consequently expansion. The resultant pressure wave is recorded by a microphone in an acoustic resonator.

MEXA
Particulate matter is collected using a 47 mm filter holder, with a similar sampling system to the standard gravimetric system. Before the sampling begins the filter is heated to approximately 900^{o}C to oxidise any 'background' material on the filter.

A process of vaporisation, oxidation and reduction is used to measure the mass of the PM components. First the filter is placed in a furnace (980^{O}C) in a nitrogen gas flow. The SOF component vaporises, is oxidised and detected as CO_2 using NDIR. The sulphate component is reduced at high temperature and detected as SO_2, also using NDIR. Next oxygen flows through the furnace oxidising the carbon trapped on the filter, which is then detected as CO_2.

CPC
A condensation particle counter (CPC) operates by condensing butanol vapour onto any particle, regardless of composition, to grow the particles to a size where they can be counted by an optical particle counter incorporated in the instrument.

In count mode the enlarged particles pass through a laser beam and the light scattered by them is collected and focussed in a photodetector. However, only one particle can be detected at any one time. This requires a very dilute sample. In opacity mode the CPC detects the light scattered simultaneously by all the particles within a volume of air and converts this to a particle concentration using a calibration function.
owever, only ne particle can be detected at any oen time/ this requires a very dilute sample. In opacity mode the CPC detects the light scattered simultaneously by all the particles within a volume of air and covnerts this to a particle concentration using a calibratuion fucitons.

There are several models available. TSI model 3010, for example, operates in single count mode only (no opacity mode), detects particles in the size range 10 nm (with 50 % efficiency) to in excess of 3µm diameter. Response time is less than 5 seconds for a 95 % concentration step change.

Electrical Diffusion Battery
A corona discharge is used to produce small ions, which attach to the aerosol particles by diffusion. The particles pass several series of electrically insulated screens to which they eventually attach by diffusion. Smaller particles have a higher diffusivity and are therefore removed earlier than large particles. The particle charge is captured and amplified for each series of screens and a backup filter. From the electric currents the parameters of a monomodal or bimodal lognormal distribution function are calculated. The sum of all currents represents the active surface of the particles.

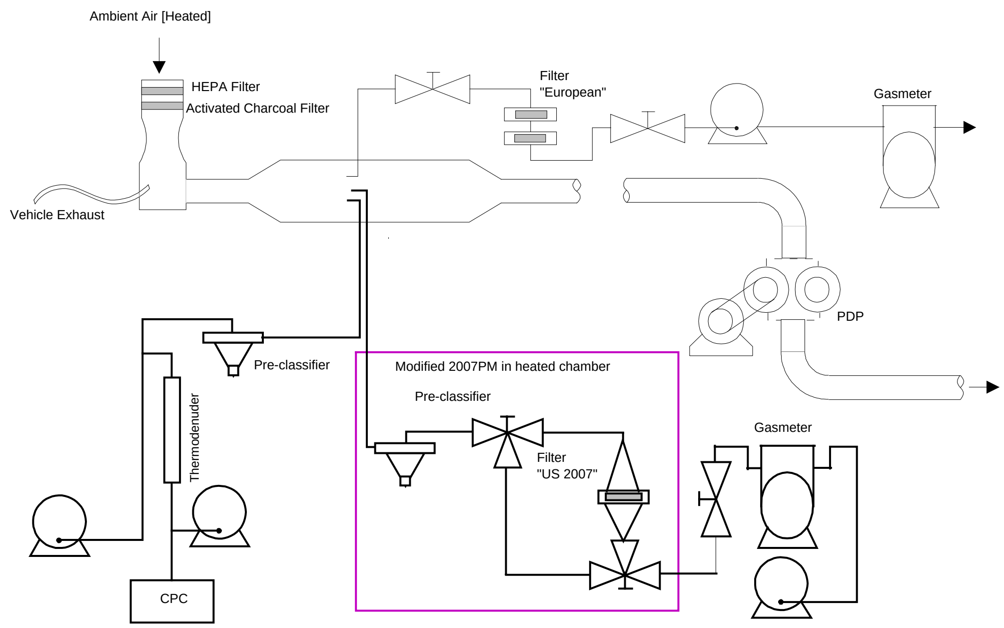


Figure 1a: Indicative Instrument and System Set-up (Light-duty).

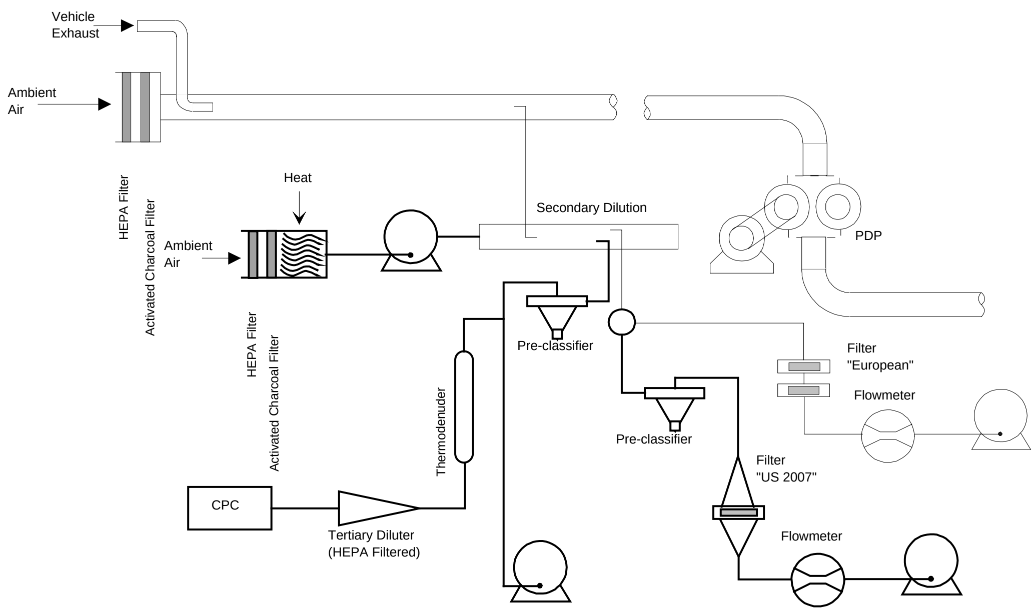


Figure 1b: Indicative Instrument and System Set-up (Heavy-duty).

Figure 2: Particle Composition for Selected Steady State Operating Conditions (Heavy Duty)

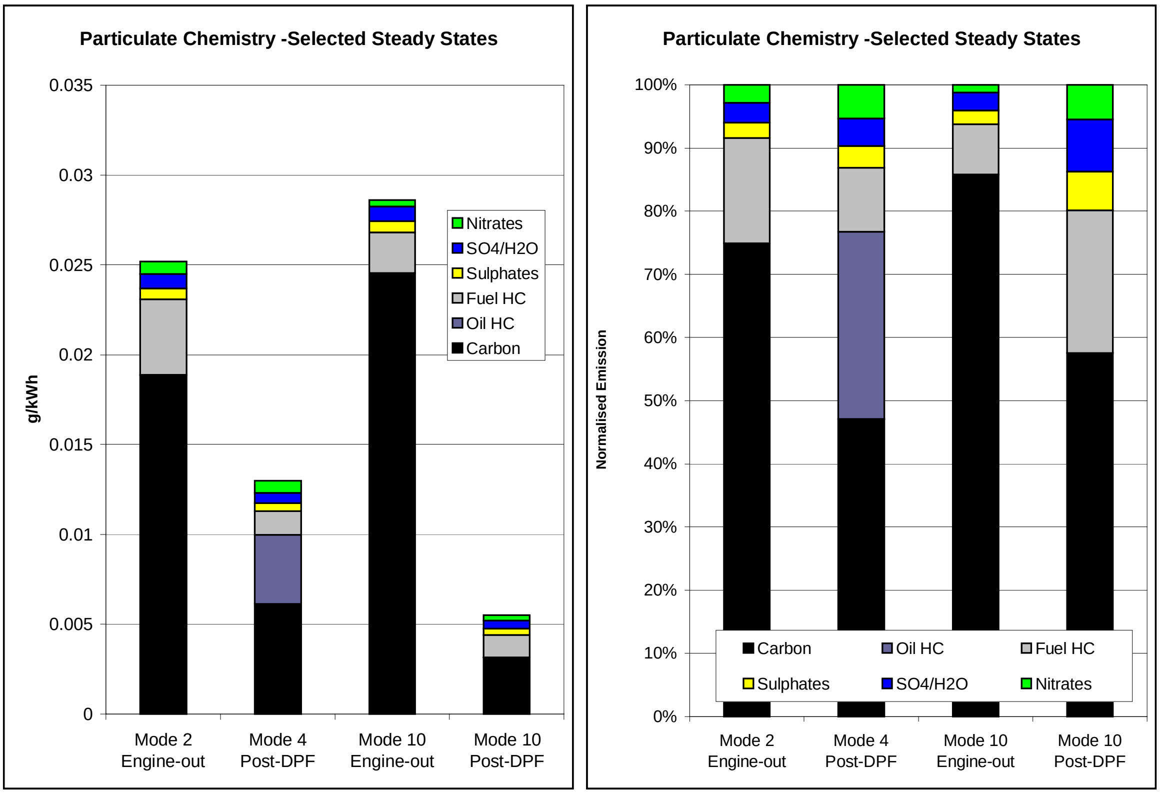
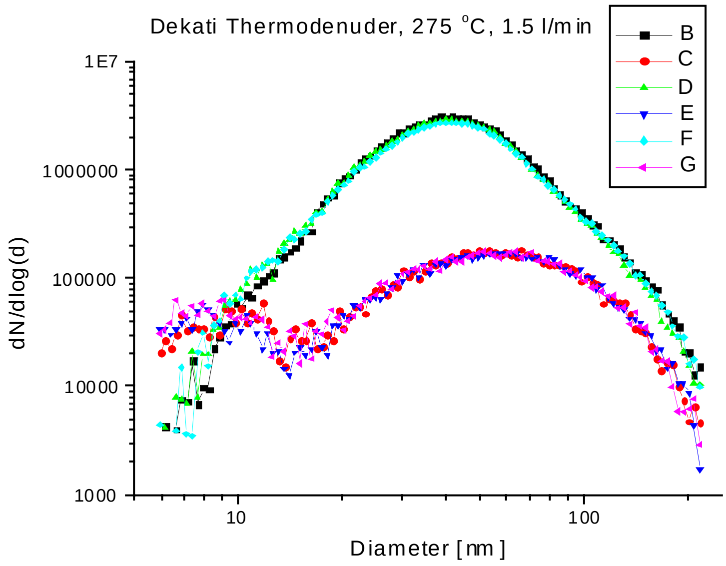
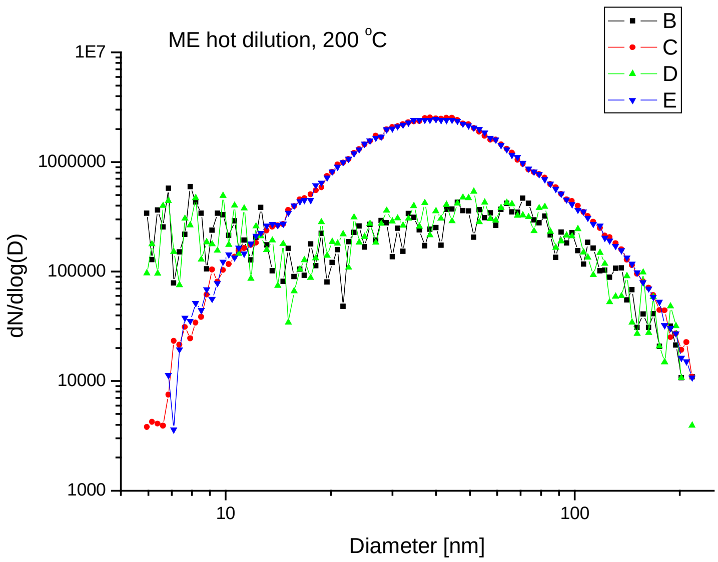


Figure 3: Size Distributions Before and After a Thermodenuder and Thermodiluter



Size distributions before and after the thermodenuder.

Curves B to G were measured in 2-minute intervals; B, D, and F through the bypass, C, E, G through the thermodenuder. Note the good reproducibility of the particle size spectrum, and the peak for very small particles.



Size distributions before and after hot dilution.

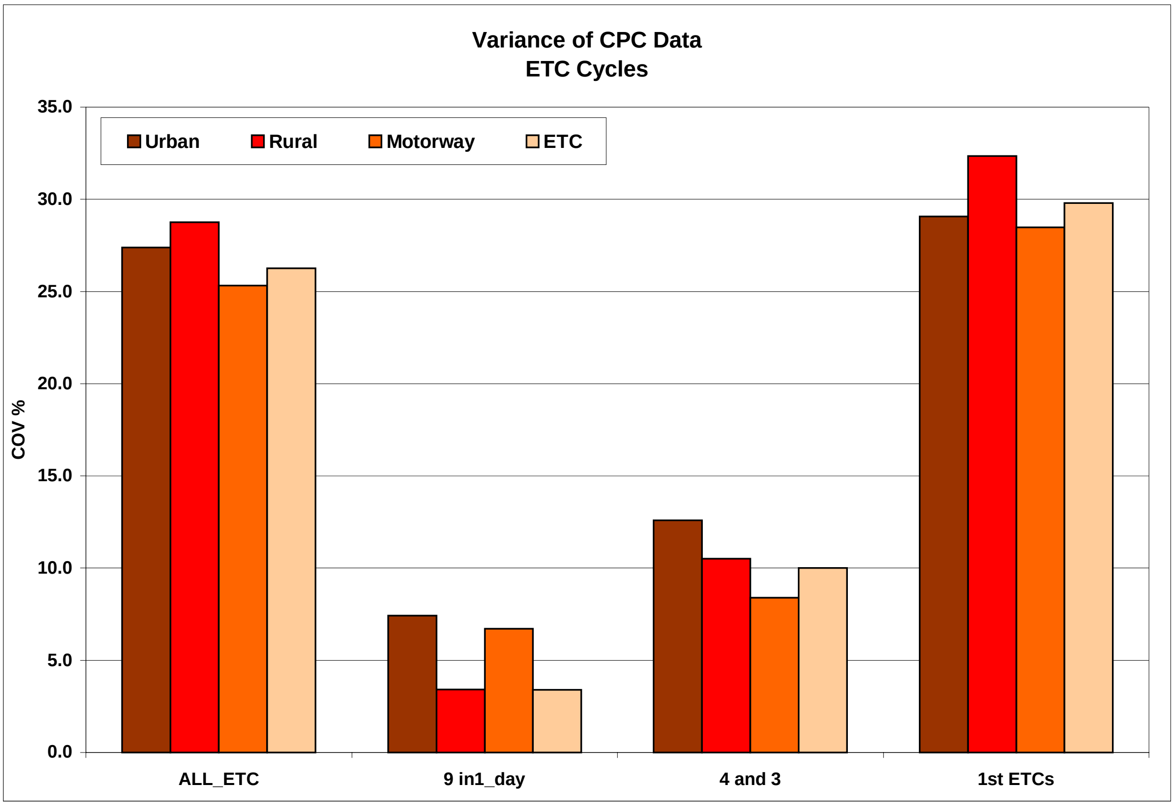
Curves B to E were measured in 2-minute intervals, B, D through the hot diluter, C and E through the bypass. The diluter of the hot dilution system is operated at a dilution ratio of 1:20. The plotted data are corrected for this dilution.

Again a peak for very small particles is observed.

The post thermodenuder and thermodiluter samples have a high number of very small (<15nm) particles that are not observed without the simple treatment. The nature of these particles is unclear. It has been suggested that the volatile material condensed on small solid particles are removed by the treatment device, leaving the very small core.

It should be noted that the thermodenuder and thermodiluter were tested under extreme operating conditions, known to produce a large number of nucleation mode particles. These very small particles might not be observed under other conditions.

Figure 4 : CPC Measurements over the ETC Cycle - COVs



This figure shows the COVs for the total number of particles over the ETC cycles for a HD engine. It demonstrates that the COVs from measurements undertaken within a single day are good (3.4% for the ETC), and that repeatability across 2 days of measurements (4 tests on one day, three tests on another) is still good (10%). However the COVs for the first test of each day is 30%.

It is thought that the day to day variation may be due to variation in the concentrations of particles entering the dilution system during the test. If the source of these additional particles can be identified and eliminated, the repeatability of ETCs over multiple days may be increased to those levels observed in a single day.

Figure 5: Inter-laboratory Comparison for a Diesel Car using ELPI + CVS + Hot Dilution