PARTICULATES

Characterisation of Exhaust Particulate Emissions from Road Vehicles

Deliverable 2:

Vehicle exhaust particulates characterisation, properties, instrumentation and sampling requirements

Version 1.1 – 01/2001

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1. Introduction

1.1. Goals of the project

The project targets to add knowledge and understanding of the emissions of particulates from the motor vehicles. A review of currently used instrumentation and sampling techniques is made. A harmonised sampling protocol for the definition of exhaust particulate sampling conditions is developed. This protocol is based on the review and knowledge of the participants and it accounts for the existing instrumentation. The developed protocol is then used in a detailed measurement campaign. This campaign will cover most of the existing and near future fuels and vehicle technologies. As a result of this campaign a database containing appropriate emission factors for particulates and other unregulated pollutants associated with them should be developed.

Deliverable 2 is the output of WP200 of the project. It aims to review the instrumentation and sampling techniques used so far for particle characterisation and provides an outline of the tools and methodology to be followed towards the completion of the project.

1.2. Background

The effect of particulate emissions on health has been of great interest for many years. Legislation on particulate emissions is based in particulate mass, either total suspended particulate mass (TSP) or PM_{10} (mass fraction of particle sizes below 10µm). Recent toxicological findings have however suggested that the adverse health effects may not only be dependent on total particulate mass. Smaller particles are believed by some to cause more adverse effects than large particles. This has lead to revision of PM Air Quality Standard in the U.S.A. The European Commission has recently adopted a new Council Directive 1999/30/EC relating to limit values for a series of air pollutants, including particulate matter, in ambient air. In parallel, particle emissions legislation has been adopted to further reduce particle emissions from mobile sources. In 1998, the European Council of Environment Ministers reached a political agreement on the final Euro III standard (amendment of Directive 88/77/EEC) and also adopted Euro IV and V standards for the year 2005/2008. For these purposes and also for understanding the mechanisms behind the adverse health effects more information on particulate characteristics emitted from motor vehicles is needed.

In recent years, it has been recognised that a large proportion of particles emitted from vehicles lie in the ultra-fine region (defined here as < 100 nm diameter (effectively PM0.1). Vehicle emissions may contribute up to 85% of particle number in urban areas and hence existing regulated mass measurements may no longer be appropriate, particularly where there is a requirement to improve source apportionment of particles by measurements of physical or chemical composition . This has led to speculation that future emission or air quality legislation may incorporate particle size criteria, limits on particle number or surface area concentration, or limits on specific chemical components of the emitted aerosol.

Over recent years, EU and US Federal government regulations have sought to limit emissions from internal combustion engines, with particular emphasis on diesel engines. These regulations have been successful in reducing diesel particulate matter emissions (DPM) by mass but laboratory tests of low-emission engines in the US (Bagley, et al. 1996) have shown that a prototype, low-emission engine produced increased numbers of nanoparticles when measured under typical laboratory conditions. However it is unclear whether this increase was due to the engine or to the laboratory test conditions.

Of all the regulated automotive emissions, vehicle particulate emissions (VPEs) are most difficult to quantify as they comprise a complex mixture of particles of varying size and composition, each of which may be influenced by many external factors including engine technology, fuel composition, after-treatment and the act of measurement itself. Comparison of particulates data from different sources is complicated by the lack of standard methods for diluting, sampling and measuring the size distribution of diesel exhaust aerosol.

Particle characterisation from vehicle emissions is a comparatively new field, which has originated in response to concerns with the health effects of inhaled particles in the ambient environment. Inhalable particles are commonly referred to as PM_{10}, that is, particles smaller than 10 µm aerodynamic diameter. New air quality standards for PM_{10} have been promulgated in the EU and US in response to concern over health effects attributed to particles. Further initiatives on PM2.5 are under review. In the EU, the Daughter directive sets targets for PM_{10} for 2005 and 2010, but these are subject to an on-going review process.

1.3. Current status

Regulated particulate emissions are currently measured using a gravimetric procedure. Particulate mass is sampled on a filter paper and the collected mass is then weighed. Measurements are done from a standard dilution tunnel with a regulated method. Measurement of particle size distribution and number concentration is a relatively recent development and no established procedures exist for instrumentation, sampling and test procedure. Most of the studies regarding size distribution and number concentration have been done from the standard dilution tunnel using different instruments. Instrumentation and sampling protocol for these studies has been selected on the basis of availability and the suitability to the scientific goals of the studies. No general agreement on formalised standard procedures or recommended methodologies exist at the moment.

Much of the current interest in further characterisation of particulate emissions arose from Bagley *et al*, 1996) who described an increase in the formation of nanoparticles in a new technology engine, where particle mass emissions were being reduced.

1.3.1. Testing programmes – Vehicle and Fuel Technologies

A number of comprehensive test programmes of sizing and measurement of vehicle particulate emissions have been conducted, both for Diesel and gasoline engines. Significant programmes reported include those conducted by the UK Department of Environment, Transport & the Regions in association with the Society of Motor Manufacturers and Traders (Moon & Donald, 1997), CONCAWE, the oil industries' association for environment, health and safety (CONCAWE, 1998), ACEA, the Association of European automobile manufacturers (ACEA, 1999), VERT, European joint project to reduce diesel engine emissions (Mayer et al. 1998, Mayer et al., 1999) and DETR/CONCAWE/SMMT Particle Research Programme (Andersson et al., 2000, Wedekind et al., 2000). Most have focused on the influence of changes of fuel and engine technologies on particle emissions.

In Moon & Donald (1997), nine light- and heavy-duty vehicles and engines were tested under steady-state and transient conditions. SMPS measurements generally showed a single peak in the particle size distribution in the range 16-270nm (0.016-0.27µm). The peak height and position varied with engine load and speed and with engine technology. For light-duty vehicles, an old high-mileage IDI diesel produced the highest particle fluxes, while a modern three-way catalyst petrol car gave fluxes 2-3 orders of magnitude lower. The effect of fitting an experimental particulate trap to a modern truck engine was to reduce its particle flux by up to 4 orders of magnitude.

The study concluded that:

- The SMPS could be used as a reliable technique for sizing exhaust particulates under steady-state conditions with a high level of repeatability;
- further work was required to validate techniques for correlating quantitatively the regulatory measurement of particulate mass with number-based and mass-based size distributions;
- further work was also required to refine and validate techniques for compositional analysis of exhaust particulates, especially from low-emission vehicles and engines;
- design features of the dilution tunnel for emissions testing of light-duty vehicles gave a low collection efficiency for particles above 2-3 µm in size;
- modern light-duty vehicle/engine and fuel technologies and the new particulate trap technologies could substantially reduce emissions of sub-micron exhaust particulates.

CONCAWE tested four Diesel and three gasoline vehicles, covering a range of technologies. with three diesel and two gasoline fuels under steady-state and European driving cycle conditions. A number of measurement techniques were used but data reported were derived mainly from SMPS measurements.

The CONCAWE study concluded that for diesel vehicles the total number of particles emitted was remarkably consistent regardless of technology changes, fuel or driving conditions. Gasoline vehicles emitted much lower numbers of particles than diesel at urban speed (number and mass). At highway speeds however, the difference between gasoline and diesel vehicles was smaller, because of a large increase in the number of particles emitted from the gasoline engines. Following investigations showed these gasoline ‘particles’ to be largely volatile. The effect of these emissions on human exposure and health remain unclear.

No clear differences were seen between the two gasoline fuels tested. In terms of particle number emissions, the differences between the diesel fuels were also not statistically significant. This included the Swedish Class 1 diesel fuel, which emitted significantly less mass than the other fuels. Although the total number of particles emitted from the diesel vehicles did not change significantly, the associated size distribution was affected by technology.

It was recognised that characterisation of particle number and size was more complex than total mass measurement, especially for transient tests, and that the repeatability of measurement techniques was not as good as for total mass measured by filter paper.

Further work was recommended on the sampling, calibration and standardisation of these measurement techniques.

The ACEA programme measured particle number, mass and size distribution of fifteen light-duty vehicles comprising ‘current’ and ‘new’ technology Diesel vehicles and current gasoline vehicles with measurements conducted on the New European Driving Cycle and steady state points at 50 and 100 km/hour. Nucleation mode particles were not detected under the testing conditions used in this study.

The study concluded that:

- Current and new technology Diesel vehicles emit particles in the same size range.
- New technology Diesel vehicles at steady state emitted on average fewer particles than current technology Diesel vehicles (~45% reduction at 50 km/hour, ~22% reduction at 100 km/hour).
- New technology Diesel vehicles have reduced regulated particle mass emission.
- That measures taken to reduce the Diesel particulate mass also decrease the particle number emission, but that a more complete understanding of the relation between particle number and mass emissions requires more research.
- For gasoline vehicles, the particle size distributions, the number emission (count) and the mass of particulates emitted are all close to or below, the detectable limit for the speeds measured.

ACEA recommended future research to:

- investigate the reproducibility of the measurement methodology across different test sites.
- adequately investigate the emissions from gasoline direct-injection vehicles.
- explore fuel and lubricant effects.
- investigate measurement principles for particle size measurement during transient tests.
- investigate the effects of the dilution ratio on the particle size and number.
- attempt calibration of measurement equipment traceable back to international standards.
- investigate alternative measurement techniques.

These studies remain internally consistent but care should be taken as to their interpretation in absolute terms until uncertainties over the significance of the nuclei and accumulation mode CVS measurements are resolved.

The VERT programme focused on off-road and heavy duty engines and studied the effect of particulate traps, reformulated fuels, engine tuning and catalytic converters to particulate emissions. The aim was to reduce emissions to comply with occupational health legislation.

The study concluded that:

- Although the new engine designs have clearly reduced the total emitted particle mass, the number of small particles emitted is not reduced.
- Further developments in engine combustion, reformulation of fuels or after-treatment through oxidation catalyst are not very promising ways to reduce fine particle emissions.
- Diesel traps were very effective in reducing the number of emitted particles.
- Gravimetric evaluation of filtration efficiency of traps is inappropriate due to false assignment of the condensable material.

DETR/CONCAWE/SMMT Particle Research Programme aimed to investigate the changes in mass and number based heavy duty diesel engine particle emissions with respect to various test conditions, engine technologies and fuel specifications. Three heavy duty diesel engines representing Euro I, II and III technologies were tested with three different fuels. Fuels included UK ultra low sulphur fuel, EN590 and Swedish Class I fuel. In addition to regulated emission measurements, Scanning Mobility Particle Sizer (SMPS) and MOUDI-impactor where used for size distribution measurement. Samples were taken from the conventional CVS type dilution tunnel, with the additional inclusion of secondary dilution.

Conclusions of the study:

- None of the tested engine technologies or fuels reduced particle mass, nanoparticles and accumulation mode particles concurrently at all test conditions.
- Engine effects were larger than fuel effects for accumulation mode and particulate mass
- Fuel effects were larger than engine effects for nucleation mode.
- Reductions of total number of emitted particles were observed for several fuels and engine technologies, but reductions were relatively small.
- Significant relationship exist between nanoparticle formation and carbon production. At reduced carbon levels nanoparticle mode become dominant.
- Nanoparticle mode is more sensitive to sampling and test conditions than the accumulation mode.
- Engines optimised for low mass emissions may not produce the lowest number of particles.

1.3.2. Testing Programmes – Measurement Techniques

Existing measurement procedures for particulate emissions, as defined in current legislation, do not explicitly aim at the collection of particulates within a defined size range.

As more information from particulate studies has emerged, the possibility that vehicle particulate emissions will need to be regulated with regard to both particle size and number, in addition to particle mass, has been discussed. DG Environment commissioned a study to investigate how such measurements might be made with respect to future type approval tests. The full report is available on-line at http://europa.eu.int/comm/dg11/pollutants/ and is titled Experimental assessment of particulate measurement instrumentation

A literature review led to the following recommendations:

- Particle emissions to be classified as <300nm and >300nm for this study. 300nm was chosen due to its significance in lung deposition. It was recognised that future health data may require this cut-off point to be changed.
- The Scanning Mobility Particle Sizer (SMPS) was recommended as a baseline technique with which to compare the simpler condensation nucleus counters (CNCs) for measuring particle numbers.

A subsequent experimental programme then assessed the recommended particulate measurement techniques. Regulatory emissions, temperatures, and smoke were also measured. The particle measurements were made with a wide range of dilutions and from raw exhaust. High temperature sampling was also investigated. For each of these sampling schemes, hot and cold start steady state cycles, hot and cold start NEDC (New European Drive Cycle) and FAS (Free Acceleration Smoke) tests were performed.

- Multiple runs gave a good indication of the reproducibility of the measurements.
- It was found that sampling method had an insignificant effect on the particle measurements, so the use of standard CVS conditions was recommended.
- The CNC data agreed well with the SMPS measurements for most conditions. However, at high speed (~120kph) the CNC gave many more particles than SMPS. These appear to be very small particles below the range of the SMPS (<7nm).
- There are no significant numbers of particles above 300nm, so it was recommended that the CNC be used without a size cut-point.

- The use of an Andersen impactor showed that there is significant mass of particles both above and below 300nm. However, the impactor was unable to sample sufficient volume to provide reliable mass data from diluted samples and only gave reproducible results when sampling from the raw exhaust.
- The Andersen impactor gave poor results due to the small mass samples collected. Improvements in impactor design and sampling volumes are necessary to make this a practicable technique for diesels.
- There was no obvious reason for changing the test cycle from the cold start NEDC. Other cycles related well to each other apart from the FAS tests, which did not appear to correlate with more realistic driving conditions.
- Older technology vehicles tended to give higher emissions of smoke, CO and THC, but particulate mass from the NEDC did not seem to relate to technology. Particle numbers were very similar for the NEDC for all vehicles studied. In other words, improvements in particulate mass emissions do not necessarily lead to particle number reductions.

Dickens *et al*, 1997 tested five candidate particle sizing instruments (SMPS, ELPI, TEOM, QCM and Andersen MKIII cascade impactor) suitable for vehicle particulate emission studies using both laboratory calibration and measurements of steady-state and drive cycle emissions on a light-duty and heavy-duty CVS .

The study concluded that:

- The SMPS provided excellent number mode particle size data over steady state tests, but there were limitations over drive cycles, with multiple runs are required to build a complete picture.
- The ELPI, although at an early stage of development, was deemed more suitable for real-time transient cycle measurements for number distribution although some problems were observed with respect to accuracy for size and concentration measurements.
- The Andersen impactor provided a low cost method of determining particle mass distribution above 400nm, providing good samples for compositional analysis.
- The TEOM provided indicative mass concentration real time data over drive cycles, but real time detail may be lost because of smoothing, and the total mass figures may not agree with regulated filter sample estimates of total mass.
- There was evidence of bad coupling between diesel particles and the QCM stages. Charge equilibration had no effect. Thus the QCM was deemed unsuitable for vehicle emission particle sizing.

Overall recommendations from the programme included the use of a sampling column to allow isokinetic sampling with minimum transport losses for multiple instruments.

- Steady-state particle number size distributions should be measured using the SMPS.
- Drive-cycle particle number size distributions should be measured using the SMPS with multiple cycles to measure up to five sizes. At least three of these sizes should be common for all vehicles/engines and fuels tested, with one or two extra sizes measured where steady-state data show that the three fixed sizes will not cover all major peaks. Suggested values for the three fixed sizes are 25nm, 60nm and 100nm.
- Mass mode measurements over both steady-state and drive-cycle tests should be measured by the ELPI in mass mode (or an equivalent gravimetric low pressure impactor) and/or by the Anderson Mk III impactor.

- The ELPI should be run along side the SMPS for both steady-state and drive-cycle tests if the ELPI number-mode calibration issues have been satisfied. Due to its real time, multi-size measuring ability, the ELPI has the potential to provide more information than the SMPS. Together the ELPI and SMPS will provide complimentary data.

1.4. Particle characterisation challenge

PM emissions from cars are legislated with respect to g/km but for heavy duty engines g/kwh is used. And when it comes to environmental legislation there is a reference to particle size as PM10 and PM2.5 are being used.

However in view of the pressure on air quality standards, and the estimated contributions of vehicle emissions to pollution, regulatory bodies are considering the need to account for particle size in future vehicle emission regulations. As a precursor to this process, studies are required to assess the capabilities of currently available particle size distribution measurement techniques in order to establish the validity of past and current assessments of the effects of, for example, fuel, vehicle and drive cycle on particle size distribution (and perhaps composition).

Such studies are a necessary precursor to the establishment of legislation and to the specification of facilities required for type approval testing. A further requirement may be the development of appropriate, less sophisticated equipment for in-service testing. Whilst initial steps have been made towards the later objective, particulate sizing measurement technology, tailored to the needs of vehicle emissions regulations, is arguably at an early stage of evolution.

One of the most significant issues in this field is the nature of the nucleation mode particles formed as a consequence of the diluting conditions and residence time in the measurement system (Kittelson 1999). These ‘new’ particles are typically 5 - 30 nm in diameter consisting of sulphate and condensable organic material. There is an on-going research effort to determine the nature of these particles. This relates principally to determining whether they are formed in real-life roadway conditions, or whether they exist solely as an artefact of the existing sampling system. Recent studies would indicate that the nucleation mode is also detected in the roadways (Kittelson et al. 2000)

It is notable however, that anomalies have been noted in a number of reported studies, which may represent sampling and measurement system artefacts. These include :

- A study for Health Effects Institute (HEI) reported by Bagley et al, 1996 where a comparison of particle emissions of new versus old technology engine showed a decrease in particle mass but an increase in particle number in the newer technology engine.
- Work conducted at University of Minnesota by Professor Kittelson suggests formation of sub-10 nm particles in CVS system under certain conditions of residence time and dilution. This nucleation mode consists of a mixture of sulphate and condensable organic material, and is known to be volatile when heated in a thermal denuder system. A stable accumulation mode of carbon material is also observed.
- Work conducted for the VERT programme in Switzerland has also identified that a significant component of particulate generated under CVS sampling conditions is volatile and its environmental fate unknown (Mayer, 1995, 1996, 1997).
- Ford Motor Co have reported formation of sub-10 nm particles in CVS systems, depending on connecting material used in the system (Maricq, 1999).
- Measurement of particle size distributions in the ambient environment near roadways show nucleation mode peak (Harrison, 2000, Shi, 1999). However, there is no composition data at

present to determine whether these are emission source particles of sulphate and condensable organic material, from gas to particle conversion in the tail-pipe and atmosphere.

- Hall and Dickens (2000) measured high concentrations of small particles from gasoline engines operating in high speeds. They concluded that these particles are strongly linked to the temperature of the vehicle exhaust system and also to the sampling system. They also noticed deposition of material to exhaust and sampling system during cool operation. This material can then be released later depending on the temperature profile

Significant research work is underway, to better characterise such sampling and measurement systems, and this includes collaborative work between groups to better determine the key factors involved in producing accurate and reproducible data.

Key conclusions :

- Existing regulated measurements for vehicle particle emissions relate to particulate mass only.
- No published standard methods are available for sampling and measurement of nanoparticles in exhaust emissions.
- Anomalies have been observed in the relationship between particle number and mass concentrations for some engine tests
- It is not appropriate at this time to use existing methods for particle size and number distribution, other than for comparative purposes
- There have been no systematic studies of particle size distribution or alternative particle metrics for in-service testing.

Key uncertainties :

- Formation of nucleation mode nanoparticles is very sensitive to the dilution conditions. Nucleation mode particles have a small influence on particle mass, but can represent a significant component in particle number. Some of the nucleation mode particles observed in CVS tests may be artefacts. Simulation of real world conditions is a challenge which is key to real understanding of the meaning of nanoparticle measurements.

The setting of vehicle emissions regulations is a complex iterative process, which has to take account of the evolving understanding of:

- the health and environmental motivations for changes in air quality legislation;
- the timing of the introduction of changes in air quality legislation;
- the understanding of the contributions of vehicle emissions to air quality;
- the practicalities of making measurements for research, type approval testing and in-service policing;
- the practicalities and cost effectiveness of achieving the standards through for example fuel specification, engine optimisation, after treatment or traffic management;
- the evaluation of potential side-effects of proposed emission countermeasures.

In order to generate the necessary data to address the above factors much research has to be executed and the results co-ordinated.

References:

ACEA, 1999. ACEA programme on emissions of fine particles from passenger cars. www.acea.be

Andersson, J.D., et al., 2000. DETR/SMMT/CONCAWE Particle research programme: sampling and measurement experiences. SAE 2000-01-2850. Warrendale PA.

Bagley, S. T., K. J. Baumgard, L. D. Gratz, J. H. Johnson, and D. G. Leddy. 1996. Characterization of Fuel and Aftertreatment Device Effects on Diesel Emissions. Health Effects Institute Research Report Number 76, 88 pp.

CONCAWE, 1998. A Study of the Number, Size & Mass of Exhaust Particles Emitted from European Diesel and Gasoline Vehicles Under Steady-state and European Driving Cycle Conditions. CONCAWE Report 98/51. Prepared for CONCAWE Automotive Emissions Management Group by Special Task Force AE/STF-10: D. E. Hall Chairman, Brussels, Belgium, 56 pp.

Dickens, C. J., M. H. E. Ball, D. Booker, J. R. Donald, A. M. Tope and M. Hughes. 1997. Evaluation of Instruments for Vehicle Emission Particle Sizing. AEA Technology Report AEAT-1180, 69 pp.

Hall, D.E., Dickens, C.J., 2000. Measurement of the numbers of emitted gasoline particles: genuine or artefact? SAE 2000-01-2957. Warrendale PA.

Harrison RM and Turnbull AB, 2000. Atmospheric Environment, in press.

Kittelson, D. B. 1999. Review of Diesel Particulate Matter Sampling Methods. USEPA. Downloadable from WWW at Centre for Diesel Research, University of Minnesota.

Kittelson D. and Watts, W. (2000) Roadway measurements of diesel exhaust aerosols. 19th annual AAAR Conference, St. Louis, Missouri 2000.

Maricq M., Chase, R.E., Podsiadlik, D.H. and Vogt, R. 1999. Vehicle Exhaust Particle Size Distributions: A Comparison of Tailpipe and Dilution Tunnel Measurements SAE technical Paper series 1999-01-1461. Warrendale, PA

Mayer, A. et al 1995. Particle size distribution downstream from traps of different design. SAE 950373, Warrendale PA.

Mayer, A. et al 1996. Trapping efficiency depending on particle size. SAE 960472

Mayer, A. et al 1997. VERT- Clean Diesel engines for tunnel construction. SAE 970478

Mayer, A, et al., 1998. VERT: Diesel nano-particulate emissions: Properties and reduction strategies. SAE 980539, Warrendale PA.

Mayer, A., et al., 1999. Particulate traps for retro-fitting construction site engines-VERT: final measurements and implementation. SAE 1999-01-0116, Warrendale PA

Moon, D. P. and J. R. Donald. 1997. UK Research Program on the Characterisation of Vehicle Particulate Emissions. (Contract Report for the Department of the Environment, Transport and the Regions and the Society of Motor Manufacturers and Traders). ETSU-R98, 90 pp.

Shi, J.P., Khan, A.A., Harrison, R.M. (1999) Measurements of ultrafine particle concentration and size distribution in the urban atmosphere. *The Science of Total Environment.* 235, 51-64.

Wedekind, B.G.A., et al. (2000). DETR/SMMT/CONCAWE Particle research programme: Heavy duty results. SAE 2000-01-2851, Warrendale PA.

2. Road Transport Particulates Emissions in an Overall Perspective

The purpose of this short section is to review current understanding in the area of European emission inventories and source attribution to put the current project, which focuses on particles from vehicle exhaust, into an overall perspective. In addition, the key current European activities with respect to inventories and source attribution are reviewed in the light of European policy plans in the area of particulates.

2.1. Primary Sources of Anthropogenic PM in Europe

Although a number of national inventories have been developed for primary anthropogenic fine particulates (e.g., UK APEG 1999), currently the only detailed particulates emission inventory for Europe that has been developed is that by TNO (Berdowski et al, 1997). Since its publication in 1997, this inventory has been updated to reflect improvements in the underlying emission factors and activity data (Senco/DRI, 1999, Second European Auto Oil programme). Currently TNO are updating the inventory as input to the European Environment Agency's "Co-ordinated European programme on particulate matter emissions inventories, projections and guidance" (CEPMEIP). The short term aim of this project (2000- 2001) is to improve the European primary particulate matter (PM_{10} and $PM_{2.5}$) emission inventory (1995 reference year), projection data and estimation methodologies. In the longer term, the programme is designed to facilitate regular reporting of particulate emissions by Parties to the UN-ECE Convention on Long Range Transport of Air Pollutants (CLRTAP).

The timing of the project recognises the requirement for the European Commission to report to Parliament and Council by the end of 2003 on the implementation of Directive 1999/30/EC, the Directive which includes ambient air quality objectives for PM_{10}. One aspect of the report will be future limits values for particulate matter, including addressing the question of whether limit values should be set for some measure of particulate matter other than PM_{10}. Given the growing recognition of the transboundary nature of fine particulates, it will have to consider this aspect as well as the contribution of local emissions.

The Commission plans to follow this report with a second, more general report, by the end of 2004 under their proposed Clean Air for Europe Programme (CAFE). This programme, currently under discussion, will include the development of integrated strategies for tackling residual air quality problems in the European Union.

On the broader European front, the next revision of the UN-ECE Multi-pollutant/Multi effect CLRTAP protocol is targeted for 2004 and will include fine particulate matter. The extension of the existing Integrated Assessment Modelling tool (The IIASA "RAINS" model) to include fine particulates is currently underway. Early results from this work are discussed later in this chapter.

2.2. Current European Inventories-What do they tell us?

Figure 2-1 shows the source contributions in the original, as published, TNO inventory. This serves to highlight the importance of non-transport sources. These are the largest contributors to overall PM_{10}/$PM_{2.5}$ emissions and remain important even for $PM_{0.1}$. Although the focus of our current project is transport emissions, given the importance for policy of understanding all contributions to ambient levels of particulate matter, similar projects are clearly needed for the non-transport area.

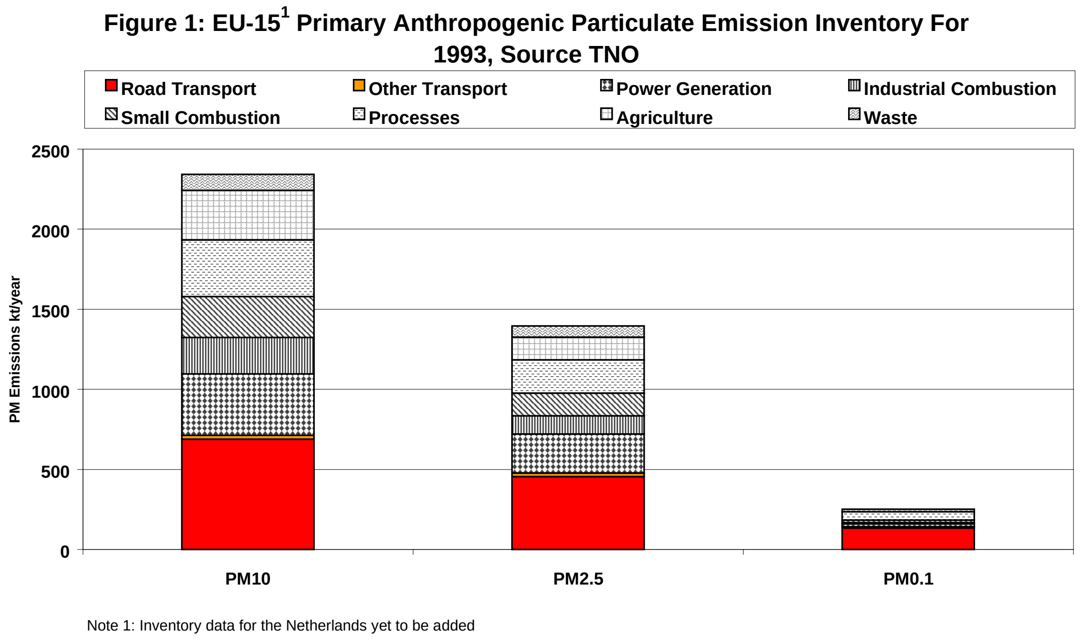


Figure 2-1:

Figure 2-2 shows the evolution of PM10 emissions in EU-15 according to the work carried out by Senco and DRI on behalf of the European Commission as part of the second Auto Oil Programme.

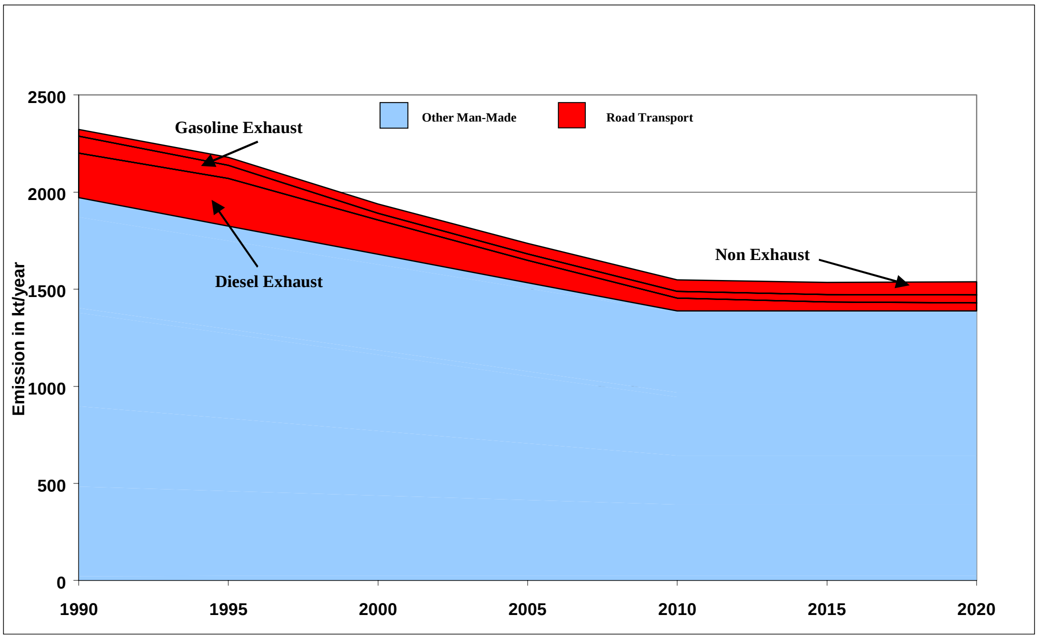


Figure 2-2: PM10 Emissions Forecast for EU-15, Second Auto Oil Programme

(Senco/DRI, March 1999)

For stationary sources, this work drew heavily on the TNO Inventory but reflects the improved understanding in some source contributions (e.g., Non-exhaust vehicle emissions, waste incineration and agriculture). In addition, the work on road transport emissions carried out under the MEET programme (the basis of the development of the COPERT 3 methodology), together with Member States fleet composition and activity data, was used by DRI to develop a more detailed forecast of road transport emissions. Comparison of the road transport emissions between Figure 1 and Figure 2 shows that DRI/Senco estimates are significantly lower than TNO. This reflects the improvement in exhaust emissions correlations (via MEET) since the TNO inventory was developed and revisions in the emission factors for tyre and brake wear.

The TNO inventory provides estimates not only of PM_{10} but also $PM_{2.5}$ and $PM_{0.1}$. Tables 2-1 and 2-2 giving the ratio of $PM_{2.5}/PM_{10}$ and $PM_{0.1}/PM_{10}$ emissions per sector and country are derived from these data. Other sources of similar data have been added to the tables for comparison purposes. As the focus for health concerns moves toward finer particles than PM_{10}, these tables, with the variability in such factors (especially for $PM_{0.1}$), highlight the need for improved data to properly inform and design rightly targeted response strategies.

Table 2-1: Ratio of Primary Anthropogenic $PM_{2.5}$ to PM_{10} Emissions: TNO vs. Others

$PM_{2.5}/PM_{10}$ 1993	Power Generation	Industrial Combustion	Small Combustion	Processes	Road Transport	Other Transport	Agriculture	Waste	Total
Austria	0.622	0.634	0.592	0.520	0.660	0.750	0.484	0.694	0.577
Belgium	0.568	0.516	0.556	0.597	0.657	0.722	0.488	0.692	0.579
Germany	0.640	0.492	0.427	0.637	0.673	0.903	0.482	0.687	0.605
Denmark	0.569	0.575	0.754	0.489	0.654	0.833	0.480	0.696	0.578
Spain	0.626	0.477	0.602	0.525	0.656	0.831	0.479	0.667	0.575
Finland	0.636	0.591	0.631	0.619	0.655	0.816	0.485	N/A	0.621
France	0.592	0.496	0.635	0.578	0.663	0.955	0.415	0.692	0.606
UK	0.563	0.518	0.499	0.593	0.653	0.909	0.419	0.679	0.577
Greece	0.647	0.514	0.658	0.415	0.627	0.818	0.426	N/A	0.592
Ireland	0.621	0.597	0.557	0.410	0.666	0.800	0.463	N/A	0.569
Italy	0.643	0.483	0.626	0.555	0.659	0.919	0.429	0.688	0.596
Luxembourg		0.547	0.594	0.642	0.658	0.917		0.685	0.626
Netherlands								N/A	
Portugal	0.626	0.593	0.751	0.409	0.664	0.905	0.450	N/A	0.571
Sweden	0.613	0.607	0.595	0.632	0.656	0.880	0.475	0.682	0.606
EU Total	0.634	0.504	0.556	0.588	0.662	0.862	0.456	0.691	0.595
UK DETR	0.509	0.600	0.444	0.644	0.852	1.000		0.818	0.645
Germany IER	0.610	0.538	0.460	0.640	0.837	0.917			0.647
IIASA	0.651			0.420	0.526	0.983	0.016		0.641

Table 2-2: Ratio of Primary Anthropogenic $PM_{0.1}$to PM_{10} Emissions: TNO vs. Others

$PM_{0.1}/PM_{10}$ 1993	**Power Generation**	**Industrial Combustion**	**Small Combustion**	**Processes**	**Road Transport**	**Other Transport**	**Agriculture**	**Waste**	**Total**
Austria	0.062	0.077	0.068	0.014	0.196	0.271	0.000	0.153	0.078
Belgium	0.086	0.047	0.077	0.168	0.197	0.222	0.000	0.154	0.115
Germany	0.029	0.026	0.022	0.154	0.192	0.484	0.000	0.146	0.085
Denmark	0.084	0.053	0.083	0.115	0.186	0.034	0.000	0.157	0.067
Spain	0.058	0.050	0.082	0.124	0.196	0.339	0.000	0.153	0.110
Finland	0.069	0.056	0.096	0.184	0.187	0.306	0.000		0.132
France	0.088	0.035	0.082	0.157	0.195	0.500	0.000	0.154	0.126
UK	0.081	0.041	0.044	0.158	0.181	0.436	0.000	0.150	0.118
Greece	0.038	0.040	0.091	0.100	0.198	0.305	0.000		0.116
Ireland	0.080	0.051	0.050	0.066	0.187	0.324	0.000		0.081
Italy	0.099	0.044	0.094	0.141	0.200	0.486	0.000	0.156	0.130
Luxembourg		0.050	0.096	0.230	0.188	0.500		0.000	0.182
Netherlands									
Portugal	0.096	0.079	0.089	0.102	0.206	0.476	0.000		0.113
Sweden	0.082	0.062	0.099	0.178	0.195	0.400	0.000	0.155	0.127
EU Total	**0.042**	**0.038**	**0.062**	**0.148**	**0.193**	**0.376**	**0.000**	**0.154**	**0.107**
UK DETR	**0.088**	**0.120**	**0.056**	**0.085**	**0.410**	**0.250**		**0.152**	

This need is further highlighted by Figure 2-3 which shows the variation in the ratio of measured $PM_{2.5}/PM_{10}$ from one London measuring station over a one year period. Although the annual average value of this ratio is consistent with the values given in Table 2-1 (around 0.6), the variation in this ratio from the hourly measured concentrations is much higher than that implied by the inventory analysis. An understanding of such variations will be crucial to the further development of both local and regional scale models used to inform future policy. The presence of values above unity also highlight some of the measurement challenges.

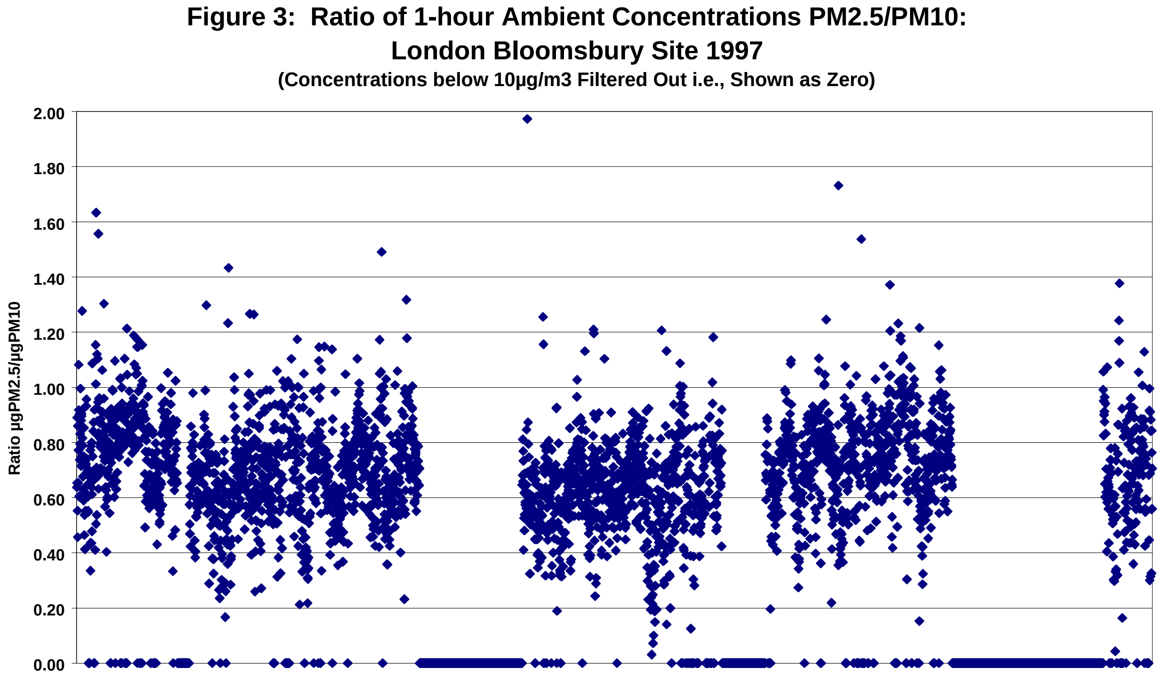
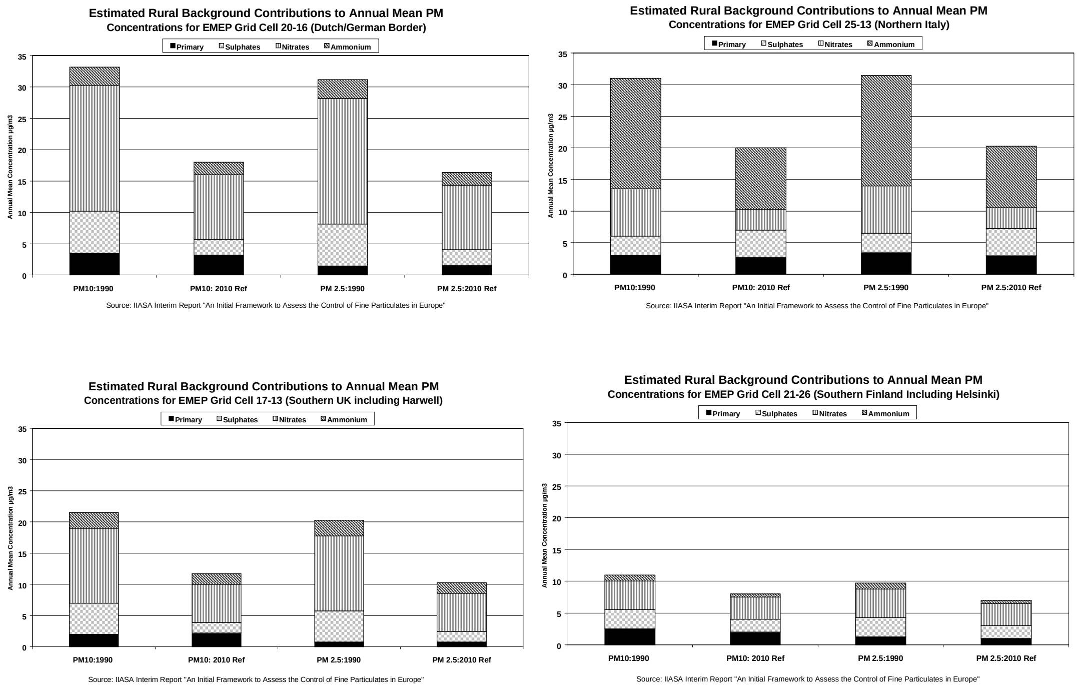


Figure 2-3:

2.3. Secondary Particulates

Work has recently commenced on understanding the contribution of secondary particles to overall particulate levels in Europe within the framework of the UN-ECE Integrated Assessment Modelling work designed to support their 2004 update of the multi-pollutant/multi-effect Protocol. This work has been carried out under the leadership of IIASA using their integrated assessment tool, RAINS. Early results from this work highlight the dominance of secondary particulates in overall rural background levels in Europe (IIASA Interim Report, April 2000). The results for four of the EMEP receptor grids in the EU are given as in Figure 2-4. In each case, the contribution of primary, anthropogenic sources is only 10 to 20%. Since secondary particulate matter is of a very fine nature, the contribution of primary sources to PM2.5 is even less. These are of course early results from the work but such a perspective on source attribution has potentially profound implications for future abatement strategies. Again, resolving the question of role of particle speciation on the health effects of fine particles may alter such a perspective.


Estimated Rural Background Contributions to Annual Mean PM Concentrations for EMEP Grid Cell 20-16 (Dutch/German Border)

Estimated Rural Background Contributions to Annual Mean PM Concentrations for EMEP Grid Cell 25-13 (Northern Italy)

Estimated Rural Background Contributions to Annual Mean PM Concentrations for EMEP Grid Cell 17-13 (Southern UK including Harwell)

Estimated Rural Background Contributions to Annual Mean PM Concentrations for EMEP Grid Cell 21-26 (Southern Finland Including Helsinki)

Source: IIASA Interim Report "An Initial Framework to Assess the Control of Fine Particulates in Europe"

Figure 2-4: The contribution of primary and secondary anthropogenic particulate matter at four EMEP Grid receptors (IIASA, April 2000)

2.4. Maximising the usefulness of the current project in the current inventory/modelling work

Given the current work on further developing emissions inventories and inclusion of such inventories into integrated assessment models, how can the current project maximise its usefulness this ongoing work? This is most probably achieved by relating the additional data that will be developed through the project to the parameters used to represent particulates in this ongoing work. For example, developing correlations for PM10 and PM2.5 and then additional correlations (if possible) which relate other size fractions, particulate numbers or speciation to these basic relationships. In practise this may prove to be an extremely difficult task but having such a perspective at the early design phase of the project should maximise the potential for such a provision.

3. Health effects associated with selected parameters of vehicle exhaust particulate

This chapter will give a short overview on health effects of exhaust particulates. It is based on reviews and conferences mentioned in the references.

3.1. Historical Perspective

Several major air pollution incidents in the 1930's and 1950's resulted in significant increased mortality in the short-term (days). Although the pollution was a complex mixture including gaseous pollutants, the role of airborne particulate matter (PM) was implicated. Recent research, first published at the start of the 1990's, raised concerns that although ambient air legislation had significantly reduced pollution levels from the 'Great Smog' days, there appeared to be a correlation between temporary increases above the current low levels of ambient air particulates and acute health effects.

Subsequently, some studies of chronic health effects linked to long-term air concentrations of PM have also been published. These studies have attempted to account for confounding factors, i.e. factors that could cause similar health outcomes to PM and therefore need to be considered in the study design, such as smoking and social status.

Whilst ambient PM levels have been reduced, the nature of ambient air pollution has also changed significantly, from predominantly industrial and home heating sources in the middle of the 20th century towards a larger share from automotive emissions in the 1990's, leaving a question mark about the comparability of the health hazards presented by current and past PM air pollution. Modelling studies investigating the contribution of automotive emissions to the total PM inventory show a decreasing trend during the current decade, highlighting a continuing change to the nature of ambient PM.

3.2. Ambient PM Health Effects

The current assessment of the role of ambient air particulate on health has largely been based on epidemiological studies in which correlation between the level of the pollutant and health effects is investigated following, where possible, allowance for confounding factors. Major findings from the epidemiological studies are:

- generally small but statistically significant links between PM mass and acute mortality/morbidity effects in some studies, with lower estimates in more recently published studies. Other studies show no effects;
- some studies have noted correlation to specific respiratory health problems, whereas others point to cardiovascular effects;
- some studies suggest fine/ultrafine PM may be more important than PM10;
- limited research to date suggests that particulate mass may not be the only criterion. Particle number distribution, surface area and/or composition may also be important; there is also possibility of interaction between PM and other gaseous pollutants in causing health effects;
- the possibility of interaction between PM and gaseous pollutants in causing health effects;

- no conclusions have been reached related to the health effects of automotive particulate emissions alone.

There has been a great deal of debate over the interpretation of the epidemiological studies. Particular concerns relate to:

- the use of ambient concentrations measured from fixed site urban monitors as a surrogate for personal exposure, where it is known that exposure is a combination of ambient, indoor, personal and occupational sources;
- the presence of co-pollutants (other gaseous species) and weather which may confound the reported results;
- the reliance on mass based sampling rather than detailed physical or chemical particle data.

Generally, it is accepted that despite the weight of epidemiological data, there is insufficient evidence to establish a causal relationship between exposure and health effects. Specifically, there are shortcomings in the studies, especially relating to consistency and unidentified confounders and the lack of plausible, fully developed biological mechanisms for the supposed effects. The search for a biologically plausible mechanism for health effects is crucial to establish this causal link between ambient particulate and health effects. Despite the lack of conclusive data on causality, the precautionary principle has been invoked in the development and implementation of emissions limits and air quality standards. Our knowledge of particle deposition in the human respiratory system, and especially how it is affected by the size and nature of specific particles, has been greatly assisted by research into aerosol dynamics and impaction mechanisms. Generally, research suggests that deposition is highest for the smaller particles which diffuse most rapidly. However, the detailed deposition characteristics of ultrafine ambient particles are unclear.

In an attempt to clarify which specific constituents or particle metrics may be most important for any health effects observed in the epidemiological ambient air studies, several groups of researchers have investigated the role of particulate characteristics:

- some have investigated the influence of carbon nuclei, particularly in the ultrafine size range, and found adverse health responses;
- there is some evidence of a role for transition metals in mechanistic studies; even though recent studies have indicated that the magnitude of such role (if existing) is likely to be small;
- there is limited information on the role of the acidic aqueous fraction;
- the formation of reactive oxygen species and free radicals in the lung may provide a mechanistic basis for effects.

Consideration of the results of epidemiological studies, inhalation investigations and chemical characterisation of ambient particulate has prompted researchers to propose various possible biological mechanisms for particle health effects. Current hypotheses suggest that the high surface area per unit mass of ultrafine particles may cause inflammation and cell damage, although as yet, no mechanism has been defined. These findings indicate that solid particles may have a very different toxicological profile than liquid particles that rapidly dissolve or evaporate after being deposited in the airways.

Recently, some authors have suggested that the observed link between ambient PM and health effects may be independent of chemical composition. It has been proposed that inhaled particles cause a prolonged inflammation response, triggering the release of free radicals and further mediators of inflammation which trigger further effects at the cellular level.

3.3. Health effects of vehicle emissions

In terms of the contribution of vehicle exhaust to the total particulate in the ambient air and in personal exposure, research has shown that this can make a significant contribution to the total respirable particulate fraction, particularly in urban areas (especially in street canyons). A greater increase is seen in the contribution to the so-called fine and ultrafine particle fractions. Based on the available health effects data, there have been few regulatory classifications/recommendations. Diesel exhaust emissions have recently been identified by the US California Air Resources Board as a Toxic Air Contaminant. In comparison with diesel exhaust, there has been limited research on gasoline exhaust. Available data on automotive exhaust emissions were reviewed by the International Agency for Research on Cancer in 1989, at which time it was concluded that for diesel engine exhaust there was ‘limited evidence’ for carcinogenicity in humans, whilst for gasoline engine exhaust there was ‘inadequate evidence’.

Major research programmes have investigated the link between automotive exhaust PM and health effects:

- occupational epidemiological health effect studies generally indicate limited correlation between exposure and effects. Furthermore exposure concentrations in occupational settings are usually significantly higher than measured in ambient air;
- some studies have provided evidence for acute effects on the respiratory function, including asthma attacks, where exhaust is thought to exacerbate rather than initiate;
- toxicological studies of health effects in animals show a range of effects, but the significance of these for low level ambient particulate exposure of humans in the environment is an area for debate.

Very little research has been conducted on the chemical nature and related health effects of automotive particulate. Analysis of the chemical composition of diesel particulates has identified the presence of PAHs and substituted PAHs, which have been suggested to be relevant with respect to human lung cancer.

3.4. Discussion

Our current understanding of the effects of particulates in the environment on human health is far from complete, particularly regarding the role of vehicle exhaust. Hence, several major research programmes are currently in progress, some of which are being overseen by the Health Effects Institute (a joint scientific initiative of the US Environmental Protection Agency and automotive industry). Recent European research has been conducted, often in international multi-centre studies such as the Air Pollution and Health (APHEA) project, the EXPOLIS project (exposure studies of city-dwelling volunteers) and the PEACE study (acute respiratory symptoms in children).

The concerns and question marks raised by the epidemiological studies have led to considerable toxicological research efforts to find explanations for the observed health effects, and to establish if they could be due to exposure to either ambient particulate concentrations or to automotive exhaust emissions or to combinations of these with gaseous air pollutants. The number of different hypotheses for the causes of the observed health effects is too large to be accommodated in a scientifically satisfactory way in a vehicle exhaust research programme because of possible conflicting sampling and analytical requirements. It is therefore necessary to select those exhaust parameters that are both feasible to measure and appear to have biological relevance. This is discussed in some detail below.

Existing regulatory controls in the European Union focus on controlling mass concentrations of PM in the inhalable and respirable ranges (i.e. PM10 - particulate matter smaller than 10 microns and PM2.5 – particulate smaller than 2.5 micron, respectively) under Directive 1999/30, and should therefore be part of the vehicle exhaust research program. A possible explanation for the observed effects at the relatively low ambient mass concentrations, a hypothesis focusing on the number of fine or ultrafine particles, rather than the mass, has been proposed. This hypothesis is supported by experimental data for some non-exhaust particulate materials, where more severe health effects are caused at a given mass concentration by the fine and/or ultrafine particles as compared with more coarse particles. Smaller particles may travel more deeply into the lungs. It has been suggested that so-called ultrafine particles, smaller than 100 nanometer or 0.1 micron are too small to be recognised by the lung defence systems and are able to pass through the lung to cause systemic health effects. To date there have been very few epidemiological studies of the relation between health effects and size-specific particle numbers to support this hypothesis. Number concentrations in size-fractions, e.g. PM_{10}, $PM_{2.5}$ and $PM_{0.1}$ would nonetheless be relevant parameters to be included in the vehicle exhaust research programme.

In addition to these physical parameters, chemical composition may be an important feature, with an emphasis on those components known to be able to produce health effects, albeit at generally much higher levels. Transition metals, and especially iron, have been implicated in the short-term health effects of ambient PM, whilst PAH has been implicated in carcinogenicity.

The composition of automotive exhaust particles is believed to vary according to particle size. The larger accumulation mode particles consist of carbonaceous material with some condensed hydrocarbons and sulphate. The smallest nucleation mode particles may in contrast consist almost entirely of hydrocarbons and sulphate.

Several organisations have conducted extensive research on the factors that influence the chemical composition of both gasoline and diesel engine exhaust emissions. Several organisations have also published results of biological tests of particulate and extracts from vehicle exhaust, e.g. to assess the mutagenic potential. There is however no agreement on the relevance to human health effects that can be derived from these tests and no such test has been validated and standardised. Therefore, it is not recommended to include this type of test in the programme.

Recommendations

The following parameters should be considered in characterising particulate emissions measured in the research programme:

- Total PM mass (measured according to present methods) with the purpose of providing basis for comparisons.
- Size fractioned emissions (e.g. PM10, PM2.5, PM0.1) to correspond with measures of exposure in health-based studies: or measured in a way that corresponds with various size modes of the combustion aerosol.
- Particle number emissions as a function of particle size distribution, including both accumulation and nucleation mode particles
- Nature and Morphology
    - Solid, liquid
    - Surface area
- Chemical Composition
    - Elemental carbon

- Total organic carbon
- Metals (in particular iron and other transition metals)
- PAH (based on Benzo(a)pyrene as a marker)
- Sulphate, nitrate

References:

EPA, 2000. Health Assessment Document for Diesel Exhaust, EPA/600/8-90/057E, July 2000, SAB Review Draft (http://www.epa.gov/ncea/dieslexh.htm)

The Health Effects of Fine Particles: Key Questions and the 2003 Review. Report of the Joint Meeting of the European Commission and HEI, 14-15 January 1999, Brussels

The Health Effects of PM2.5 (including ultrafine particles). Report 99/60. CONCAWE , 1999, Brussels

Symposium 'The Biology of Air Pollution', 25-26 October, Institute of Biology, London [Abstracts]

PM2000: Particulate Matter and Health - the Scientific Basis for Regulatory Decision-making. Specialty Conference and Exhibition, January 24-28, 2000. Charleston, South-Carolina (co-sponsored by US Environmental Protection Agency) [Abstracts]

4. Particle formation and structure.

Diesel exhaust particulates are usually agglomerated. Their core is from solid carbonaceous material and ash. On top of this core there is a layer of volatile organic and sulphur compounds (e.g. Steiner & Burtcher, 1993). In this chapter, the mechanisms of how these particles are formed are discussed. The particles undergo three basic phases:

- Formation of soot particles and volatile components in the cylinder and their processes in the tailpipe. These phases are described in 4.1.
- Exhaust dilution processes as the gas exits the tailpipe. This phase is described in 4.2.
- Atmospheric processes after the particles have mixed with outdoor air. Important as these may be, this phase is beyond the scope of this study.

4.1. Formation mechanisms

4.1.1. Diesel engines

The formation of diesel exhaust particles has been extensively studied. Below, a standard description of the formation process is described, basically along the lines drawn by Heywood (1988). Most of the solid carbon, or soot, is formed from incomplete combustion of fuel hydrocarbons. The burning is incomplete because of diffusion limited oxygen transfer to the burning fuel. Soot formation starts in the engine during the combustion process. Typical temperatures are between 1000 and 2800 K at pressures of 50 to 100 atm. Due to high concentration and high temperature, the formed carbon particles agglomerate in the engine and exhaust train and form the core of the exhaust particles. The source for inorganic ash is the small amounts of metal compounds in the fuel and lubricant oil.

The time available for the soot formation is in the order of milliseconds. The formation process starts from fuel molecule which contains approximate 12-22 carbon atoms and whose H/C mass ratio is ~0.1 (see fig. 4-1). First condensed phase material comes from the fuel molecules via their oxidation and pyrolysis products. These products typically include unsaturated hydrocarbons, like acetylene, and polycyclic aromatic hydrocarbons (PAH). These types of molecules are most likely precursors for soot in flames. The precise formation mechanism is not well known, but most probable formation rates are thermal decay of fuel molecules, polymerisation, and dehydrogenation. The formation rate depends on temperature. If the temperature is less than 1700 K, only aromatic hydrocarbons form soot through relatively fast and straight mechanism. When the temperature is higher than 1800 K, slower process is forming soot particles by breaking the aromatic rings into smaller hydrocarbon molecules which then polymerise and then form larger unsaturated molecules that immediately form soot nuclei. Aliphatic molecules can form soot only through the latter mechanism. The formed particles or nuclei are generally very small, less than 2 nm in diameter. These particles grow larger through surface growth and agglomeration. Surface growth is the main mechanism for generation of solid-phase material. It involves the attachment of gas-phase species (e.g. PAHs and polyacetylenes) to the surface of particles. In surface growth the number of particles stays the same but the amount of soot increases.

The very high concentration of particles in the cylinder leads to their agglomeration (coagulation) as particles collide with each other due to their random relative motion. Coagulation and oxidation result in the significant reduction of the particle number concentration at the latest stages of the in-cylinder combustion (Kittelson et al. 1992). In agglomeration particles collide and coalesce due to high concentration and temperature, decreasing the number of particles but increasing their size. The total mass of the particles is constant during pure agglomeration. Some heavier hydrocarbons bind the agglomerates together. Agglomeration of particles continues even after the surface growth stops.

At each stage of this formation process oxidation can occur and soot is burned in the presence of oxidising species. The eventual emission of soot from the engine will depend on the balance of formation and burnout. Figure 4-1 shows a schematic diagram of the formation processes.

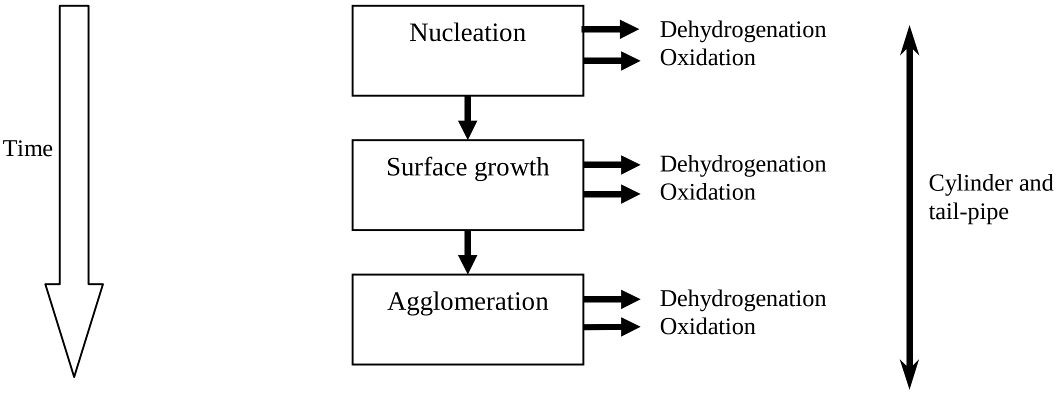


Figure 4-1: Particle formation mechanisms. (Adapted from Heywood, 1988)

The volatile organic material originates from a fraction of unburned fuel, evaporated lubricant oil and combustion derived hydrocarbons. This fraction consists of small quantities of poly-cyclic aromatic compounds, some of which may contain oxygen, nitrogen and sulphur. Sulphates originate from the small fraction of sulphur in the fuel that is oxidised to SO_3 and converted to sulphuric acid when combined with water. In addition to these main components small trace amounts of different metals, phosphorous and calcium have been found in particulates. These compounds originate primarily from lubricant oil but also from some fuel additives.

4.1.2. SI engines

Particles from spark-ignition engines are generally less well understood. With carburation or port injection, the fuel and oxygen are much better mixed than in diesel engine, and consequently particle mass emissions are several orders of magnitude lower than for diesel. Spark-ignition engines can have three kinds of particulate emissions: organic particulates including soot, sulphates and lead. The organic particles are primarily soluble organic material. However when using overly rich or lean mixtures soot emissions can occur. Lead particles are not anymore a significant problem because unleaded gasoline is increasingly used world-wide.

The recently introduced gasoline direct injection (GDI) engines sacrifice fuel-oxygen mixing for better economy, conceivably leading to particle formation process similar to diesel engines. Particle emissions comparable to diesel engines have indeed been measured (Graskow et al. 1999, Hall and Dickens, 1999).

4.1.3. Tail-pipe processes

If the number concentration of soot agglomerates is high or if the residence time is long enough in the exhaust system, some coagulation of the agglomerates can take place and larger agglomerates are formed after particles have left the engine. Formed agglomerates can be treated as fractals, thus it is possible to derive their fractal dimension which gives information of the compactness of the agglomerate (Forrest and Witten, 1979, Samson et al., 1987). Fractal dimension is a quantity, which scales the mobility equivalent size of the particle and its mass. The fractal dimension can have values from 1 to 3. The looser the structure of the agglomerate, the lower the fractal dimension is. If the particle is a sphere its fractal dimension is 3. Typical values of fractal dimensions for diesel agglomerates are 2.4-2.8. Usually some hydrocarbons and other volatile materials form a layer around the carbonaceous agglomerate.

Significant sulphate emission can occur with oxidation-catalyst equipped engines. Sulphur from the fuel is oxidised within the combustion chamber to sulphur dioxide, SO_2. This can further be oxidised to sulphur trioxide which is further transformed to sulphuric acid when combined with water. This sulphuric acid can form particles through nucleation. In addition to sulphur content of the fuel, levels of sulphate emissions depend on the operation conditions of the vehicle and the details of used catalyst system.

If the exhaust pipe is cold, as is the case in cold start, processes similar to those described in the next chapter may conceivably take place, but there is insufficient information of the importance of such phenomena.

Possible after-treatment systems also affect the emission. Diesel traps and filters reduce the amount of carbonaceous particles while catalysts remove mainly organic compounds (e.g. Mayer et al., 1998).

4.2. Aerosol processes during dilution

Dilution takes place in atmosphere as the exhaust gas exits the tailpipe and is mixed with the ambient air. In dilution, the concentrations of particles and gaseous components decrease. Mixing with cool ambient air also decreases the temperature of the aerosol. The same process also takes place in various dilution schemes used for exhaust particle measurement. The description here should apply to both atmospheric dilution and dilution systems, as long as the local dilution rates and temperatures are the same.

The dilution effectively freezes the soot particle size distribution against agglomeration, as the particle concentration falls down. However, a number of other processes may take place when exhaust gases cool and dilute with air (see fig. 4-3):

- nucleation, or formation of new particles
- condensation, adsorption, and absorption of gas phase components on particle surface
- structural changes of agglomerates

These changes depend strongly on conditions of the environment and the aerosol. Temperature, humidity, dilution ratio and rate, concentration of volatile material and number of soot particles affect the nature of changes during ageing. Usually the end result is combination of the different mechanisms.

4.2.1. Nucleation

The process having the strongest effect on number size distribution is nucleation, or formation of new particles. In nucleation, number count increases rapidly and easily produces particle counts of few millions in cubic centimeter. If nucleation occurs the number of nucleated particles usually overwhelms the number of coagulation mode particles.

In atmosphere the conditions can favour nucleation and nucleation mode has been detected in road tunnels and in open road (Weingartner et al., 1997; Kittelson and Watts, 2000). When moving away from the traffic, particle size distribution changes, moving to larger sizes, and the total concentration drops (Shi et al., 1999). The decrease in number concentration was found to be faster than the decrease in mass concentration. In their study Shi et al. concluded that these changes are due to coagulation and dilution. Nucleation can also take place in dilution systems if the dilution ratio is small (Kayes et al., 1998) or the residence time is high and temperature low enough (Kittelson and Abdul-Khalek, 1999). Nucleation mode has been reported in CVS diluted exhaust by several authors (see chapter 5).

Experiments suggest that nucleation mode particles are totally volatile and evaporate completely when heated up to 175°C (Lüders et al., 1998). The onset of nucleation has been reported to be very sensitive to dilution conditions (Abdul-Khalek and Kittelson, 1999; Kittelson and Abdul-Khalek, 1999). As a candidate for the process, binary H_2SO_4-H_2O nucleation has been suggested (Kittelson and Abdul-Khalek, 1999, Baumgard and Johnson, 1996). To test the plaucibility of this argument, a simplified simulation was performed. The goal was to find out if the sulphur level and temperature of the dilution gas could favour nucleation. During dilution, the sample temperature was simply assumed to be weighted average of exhaust gas temperature and dilution air temperature. Dilution air was assumed to be dry. Theoretical amount of sulphuric acid required to produce $1/(cm^3 \cdot s)$ nucleation rate in diluted sample was calculated according to a paper by Kulmala et al. (1998). One should note that the parameterisation was not fitted for the temperature and nucleation range used in these calculations. Exhaust sulphur curve was calculated using 320 ppm for fuel sulphur content and assuming 10% conversion factor from SO_2 to H_2SO_4. Lambda value of 2.5 was used. An example of the results of this simplified scheme is shown in figure 4-3. The 293K curve, extending well to the left of the “critical” nucleation rate curve, would produce nucleation, whereas the 313K curve would not. Keeping in mind the oversimplification of the calculation, the main result here is that the theory can in principle explain the onset of nucleation, as well as its sensitivity to dilution parameters, in reasonably realistic conditions.

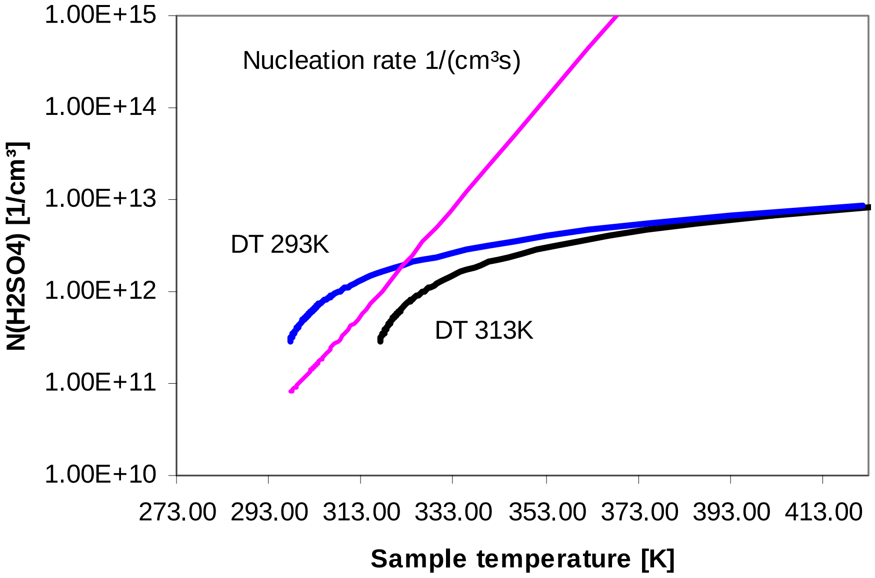


Figure 4-2. Theoretical curves show the amount of sulphuric acid required to obtain 1/(cm3·s) nucleation rate. Other curves exhibit simulated exhaust sulphuric acid concentrations with different dilution air temperatures. DR=40

4.2.2. Condensation, adsorption, absorption

In addition to homogeneous nucleation, also heterogeneous nucleation, i.e. condensation of gaseous components on particle surfaces may take place. Condensation is favoured because it requires smaller super-saturation ratio values, and consequently condensation should always take place when nucleation occurs. Condensation will lead to an increase in the mean size of existing particles.

Adsorption of hydrocarbons and sulphates on the surface of existing solid material can also be responsible for particle growth. The results of this mechanism are similar to the heterogeneous condensation but adsorption can be significant even at under-saturated conditions, since the forces involved in the surfaces of the adsorbed and the solid material are much stronger than in the case of condensation. Adsorption is considered as the main mechanism by which particles obtain their soluble fraction (Reichel et al., 1983).

Originally hydrophobic carbon black particles may absorb water at high relative humidity if the particle is covered with organic surfactants. The impact of absorbed water on total mass is generally low. Vartiainen et al. (1994) noticed total mass increase of 2-6% when the relative humidity was increased from 40-90%.

4.2.3. Structural changes of agglomerates

Condensed water vapour can shrink the agglomerates, decreasing their size and increasing their density. This shrinking is due to capillary forces induced in the particle. After shrinking, particles start to grow by condensation. Condensation of volatile hydrocarbon components during the dilution process could also lead to partial collapse of chain agglomerates (Weingartner et al., 1995, Huang et al., 1994).

4.2.4. Relative importance of processes

The necessary saturation ratio of the volatile components is lowest for adsorption. With increasing saturation ratio, the importance of condensation and nucleation increase. As described above, nucleation is sensitive to dilution ratio, dilution air temperature, and residence time. Nucleation is favoured by low dilution ratio, low temperature, and long residence time. (Kayes et al., 1998, Kittelson and Abdul-Khalek, 1999). Adsorption and condensation are competing processes for nucleation, being favoured by high available surface area of solid particles. Thus the amount of carbon particles vs. volatile hydrocarbons affect the formation of the nucleation mode. Experimental results suggest that use of particulate filter may actually cause nucleation by reducing the amount of surface area available for condensation (Lüders et al., 1998). Also absence of some chemical species, e.g. sulphur, affects strongly on formation of nucleation mode. Figure 4-3 shows the principal routes possible for gas phase components during dilution.

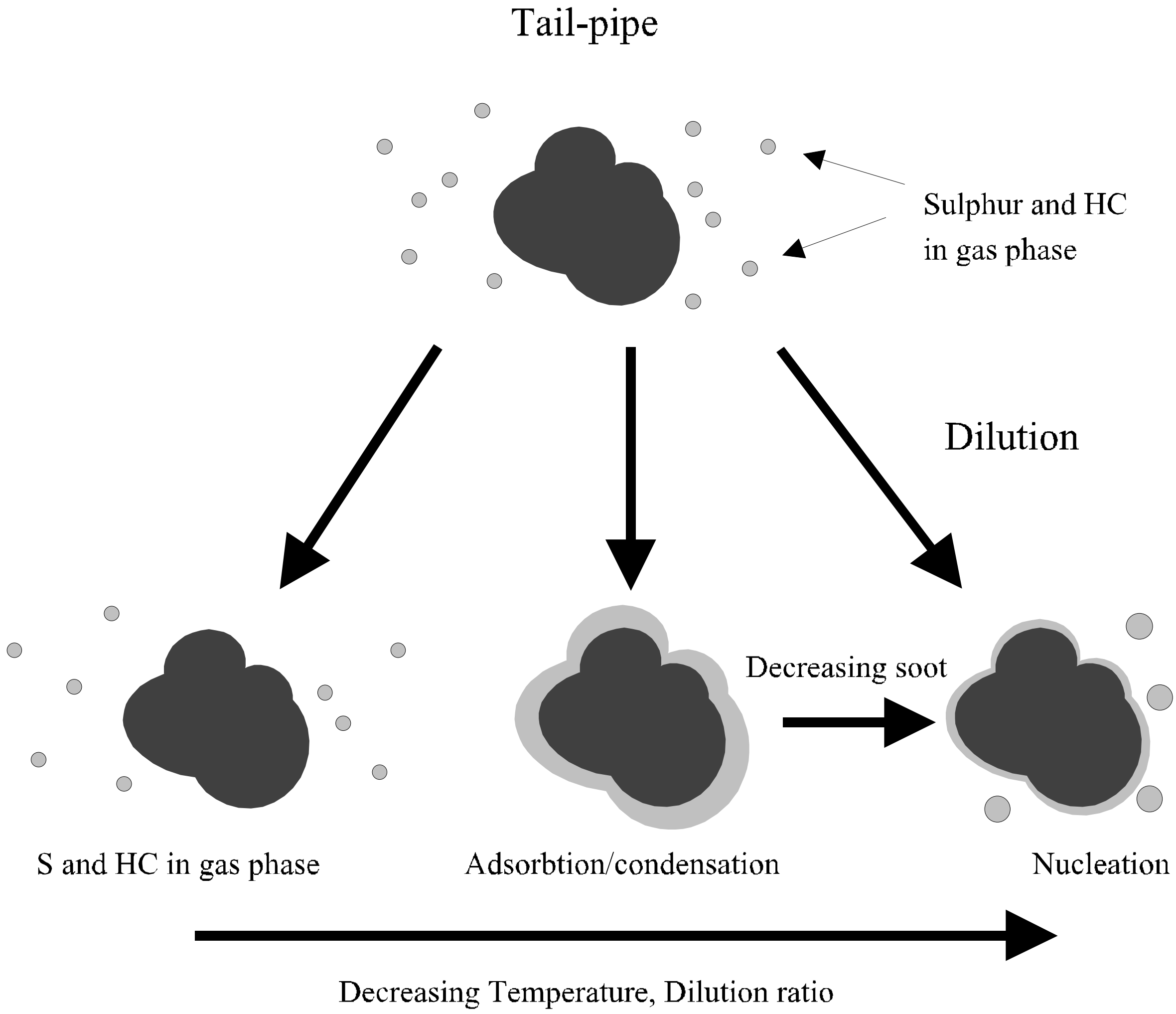


Figure 4-3: Possible routes for sulphur and volatile hydrocarbons during the dilution.

4.2.5. Particle size distribution

Typical particle size distribution of diesel exhaust is shown in figure 4-4. Modes are nucleation (D_p < ca. 50 nm), accumulation (ca. 50nm < D_p < 1 µm), and coarse (D_p > 1 µm). Most of the particle mass is in the accumulation mode between the 0.1-0.3 µm diameters. Particles in this size range are solid carbonaceous agglomerates with some adsorbed materials. This mode appears to be reproducible. The coarse mode contains 5-20% of the particle mass (Kittelson, 1998). It is believed to consist mainly of particles that have been deposited on engine cylinder, exhaust system or sampling system surfaces and later re-entrained. This mode tends to show poor reproducibility under measurement. The particle size of nucleation mode is generally between 5 to 50 nm, although smaller sizes have also been observed. The particles of this mode consist mainly of volatile organic and sulphur compounds, although some solid carbon and metal compounds can also be found. The mass fraction of this mode is small, in the range of 1-20% (Kittelson, 1998), but in some cases more than 90% of the total number of particles can be attributed to this size fraction. This nucleation mode can be reproducible but it is very dependent on the dilution and sampling setup used (e.g. Kittelson and Abdul-Khalek, 1999). Experiments suggest that nucleation mode particles are totally volatile and evaporate completely when heated up to 175°C (Lüders et al., 1998).

Particle size is an important factor influencing how the particles behave within the engine, exhaust train and environment. The size and composition of the particles also affects how they are affected by different aftertreatment devices. Diesel traps and filters reduce the amount of solid particles, mainly lowering the accumulation mode. Traps remove solid particles while catalysts remove mainly organic compounds that contribute the soluble organic fraction in the particles and the nucleation mode.

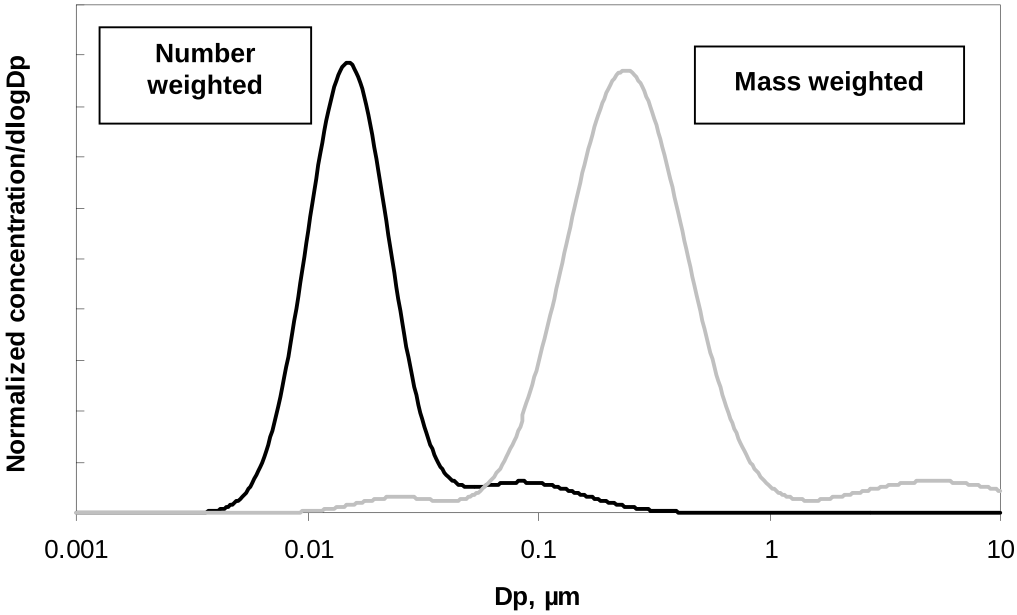


Figure 4-4: Diesel exhaust particle size distribution. Number weighted distribution with black line and mass weighted with grey line. (Adapted from Kittelson, 1998).

4.3. Non-exhaust emissions

Although non-exhaust emissions are not the focus of this project short overview is presented.

Particulate emissions from vehicles are not solely a consequence of combustion-derived exhaust emissions, and that various components can be generated from brake and tyre wear, from roadway wear, and from resuspension of dust from the roadway surface.

Emission factors have been derived for these components by USEPA, but these have generally considered inappropriate for use in Europe because of variations, particularly in climate, and roadway composition.

An alternate approach is to adopt the use of marker chemicals as specific markers of wear components; either elemental markers (heavy metals) or specific organic compounds.

Lead, iron, chromium nickel, copper , (platinum, palladium and rhodium from catalytic converters) have been suggested as markers for exhaust emissions.

Antimony, copper, zirconium and titanium have been suggested as brake wear markers.

Measurement of alumino-silicate has also been used as a dust marker., and lead has also been suggested as a marker for resuspended dust following its removal from gasoline, and hence exhaust emissions.

A recent publication by Fauser (1999) reported measurement of organic-based bitumen and tyre markers in Copenhagen. Tyre markers evaluated included zinc, organic zinc and degradation products of rubber. Bitumen markers included maltene and asphaltene compounds.

Tyre and bitumen particles each constituted approximately 5% by weight of urban aerosol; bitumen particles were associated with a mean aerodynamic diameter of 1 μm, 92% of the mass of tyre particles had aerodynamic diameters less than 1 μm, but with a smaller mode at 10 μm. These data are consistent with earlier work.

References:

Baumgard, K.J. and Johnson, J.H., 1996. The effect of fuel and engine design on diesel exhaust particle size distributions. SAE 960131.

Fauser, P. 1999. Particulate Air Pollution with Emphasis on Traffic Generated Aerosols. Risø Report No. Risø-R-1053(EN), Roskilde, Denmark

Forrest, S. R., Witten, T. A. (1979) *J. Phys. Math. Gen.* 12, L109-L117

Graskow, B.R., Kittelson, D.B., Ahmadi, M.R., Morris, J.E., 1999. Exhaust particulate emissions from a direct injection spark ingnition engine. SAE 99-01-1145.

Hall, D.E., Dickens, C.J., 1999. Measurement of the number and size distribution of particles emitted from a gasoline direct injection vehicle. SAE 1999-01-3530.

Heywood, J.B. (1988) Internal combustion engine fundamentals; McGraw-Hill International Editions.

Huang, P.F., Turpin, B. J., Pipho, M. J., Kittelson, D. B., McMurry, P. H. (1994) Effects of water condensation and evaporation on diesel chain-agglomerate and morphology. *J. Aerosol Sci.* 25, 447-459.

Kayes D., Hochgrep S. (1998) Investigation of the dilution process for measurement of particulate matter from spark ignition engines ; Sae Technical paper series 982601

Kittelson, D. (1998) Engines and nanoparticles: A review. *J. Aerosol Sci.* 29, 575-588.

Kittelson D. and Abdul-Khalek I. (1999) Formation of nanoparticles during exhaust dilution ; EFI members conference : ”Fuels, Lubricants, Engines & Emissions” ; University of Minnesota Department of Mechanical Engineering 1999

Kittelson D. and Watts, W. (2000) Roadway measurements of diesel exhaust aerosols. 19th annual AAAR Conference, St. Louis, Missouri 2000.

Kulmala M., Laaksonen A, Pirjola L ; Parametrizations for sulfuric acid/water nucleation rates ; Journal of Geophysical Research vol. 103, no. d7, 8301-8307 ; 1998

Lüders H., Krüger M., Stommel P., Lüers B.(1998) The role of sampling conditions in particle size measurements ; Sae Technical Paper Series 981374

Mayer, A, et al., 1998. VERT: Diesel nano-particulate emissions: Properties and reduction strategies. SAE 980539, Warrendale PA.

Reichel. S., Pishinger. F.F., Lepperhoff. G., 1983. Influence on Particles in Diluted Diesel Engine Exhaust Gas, SAE Paper 831333.

Samson, R. J., Mulholland, G. W., Gentry, J. W. (1987) *Langmuir* 3, 272-281

Shi, J.P., Khan, A.A., Harrison, R.M. (1999) Measurements of ultrafine particle concentration and size distribution in the urban atmosphere. *The Science of Total Environment.* 235, 51-64.

Steiner, D.and Burtscher, H. (1993) Studies on dynamics of adsorption and desorption from combustion particles, by temperature dependent measurement of size, mass and photoelectric yield. *Water, Air and Soil Pollution* 68, 159-176.

Vartiainen, M., McDow, S. R., Kamenes, R. M. (1994) Water uptake by aerosol particles from automotive exhaust and wood smoke. *Chemosphere*, 29, 1661-1669.

Weingartner E., Baltensberger , U., and Burtscher, H. (1995) Growth and structural change of combustion aerosols at high relative humidity. *Environ. Sci. Technol*. 29, 2982-2986.

5. Sampling and diluting the vehicle exhaust

5.1. Background

Particle formation and therefore chemical composition and size distribution is strongly dependent on the conditions in the surrounding environment. The ambient conditions after the tail-pipe decide the composition and structure of particle phase. However to characterise and compare emissions from different engines and vehicles some agreed measurement system and protocol is needed. This sampling and dilution system is the first and very critical part of measurement setup. In principle, the basic steps of this process involve the sampling, i.e. the extraction of a representative sample of the exhaust flow to be analysed, the primary dilution of the sample with air or any other inert gas, the possible treatment of the condensable species (removal, evaporation or oxidation) and any final dilution. This process also involves the transfer of the sample between the source and the primary dilution chamber and also between the different devices.

To be able to measure particle size distributions, exhaust gas must be in operational range of the measurement devices by temperature and particle number. This is usually realised by diluting the exhaust gas with clean air. Even if instruments are capable of measuring at hot exhaust temperatures, dilution is needed to freeze or slow down physical or chemical processes taking place in the exhaust gas such as coagulation and condensation. Dilution is also used to reduce temperature to some standard low value for comparison and representative reasons. These reasons have lead to current CVS systems.

New and better engine technologies have led to reduced particulate mass emissions. Interest has shifted to smaller particle sizes, size distribution measurement, and alternative sampling methods. These alternative methods usually use mini dilution system and sample is taken directly from the tail-pipe. Sampling from the CVS tunnel is technically relatively well understood and iso-kinetic sampling is relatively easy to achieve. The dilution ratio and sampling conditions in CVS are not so well defined, especially when driving transient cycles. In CVS sampling, increasing the load and speed results in lower dilution ratios, which does not represent the real-world case at all. Tailpipe sampling offers significant technical challenges, related to variable temperature, air flow and pressure at the sampling point, but the conditions could be better defined.

Several investigations in the past and more recently showed that the details of the sampling / transfer / dilution system (in short – sampling system) affect to a very large extent the recorded properties of the aerosol sample. This will be further demonstrated in the following paragraphs in a compact form since already a couple of reviews in the past focused in this area (Kittelson et al., 1999, DG3 Study, 2000). Therefore, aim of this section is to justify the significance of a well designed sampling system and to provide the general directions on which to base exhaust aerosol sampling and dilution.

5.2. Aerosol loss and ageing processes

5.2.1. Loss mechanisms

Particle losses in a sampling system are known to occur through inertial impaction, thermophoresis, diffusion, and electrostatic deposition on charged surfaces. These processes are relatively well understood and can be minimised in a well-designed sampling system. In addition, software is available which can aid in the design process, and estimate losses for a system. These are discussed in greater detail in Dickens et al, 1997 where a systematic analysis was undertaken of exhaust sampling systems. It should be noted, however, that losses will not be uniform but will be influenced by particle size, concentration and environmental factors such as temperature and pressure.

Phoretic forces (sometimes referred to as radiometric forces) on a particle are caused by the interaction of the gas molecules on the particle surface. Under normal conditions the time-averaged interactions occurs equally over the entire surface area of the particles and causes the particle to have a random motion (Brownian diffusion). However, there are physical circumstances that can cause a net imbalance in the number of interactions around the surface area of the particles and the result is a net particle motion in a particular direction. It is the nature of the physical mechanism that brings about this motion that distinguishes the type of phoretic force.

5.2.1.1. Thermophoresis

Thermophoresis is the motion of a particle derived from forces arising from a temperature gradient. This is an asymmetric force from more vigorous gas collisions with the particle on the high temperature side of the gradient, inducing a move in the direction of cooler surfaces. Although such forces are weak, mobility of the emitted particles is sufficiently large to make this process important. The importance of thermophoresis increases as particle diameter decreases.

Deposition of soot particles to cylinder and exhaust walls and sampling lines has been attributed to a thermophoresis, causing soot to form a layer on the cool surfaces in the vehicle and the sampling system. These sinks of soot particles may subsequently be re-entrained under changing exhaust conditions, and may account for up to 20-45% of the measured soot mass. (Kittelson, et al. 1990). Thermophoretic deposition losses can be minimised by avoiding temperature gradients in sample lines through heating or insulation.

5.2.1.2. Diffusiophoresis & Photophoresis

Diffusiophoresis occurs when there is a non-uniform mixture of gases and a gas concentration gradient is established. An example is when a vapour is produced in one location and diffuses into the surrounding air. At the same time the air will diffuse into the vapour but if the vapour molecules are heavier than the air they will impart a greater momentum to the particles in the direction they are diffusing. The magnitude of the force depends on the diffusion coefficients and molecular weights of the gases. It is approximately independent of particle size (Hinds, 1982).

Photophoresis is a special case of thermophoresis. It occurs when one side of a particle is illuminated and warmed by light. A temperature gradient is formed in the particle which is then passed on to the surrounding gas and the same mechanism for thermophoresis occurs. It should be noted that there is no overall temperature gradient in the gas. It is thought that photophoresis may be significant for the movement of submicron particles in the upper atmosphere but has no practical application size (Hinds, 1982).

5.2.1.3. Diffusion

Diffusion of particles can occur from both Brownian motion and the movement of particles down a particle concentration gradient. Particles may be lost by diffusion through the boundary layer to the walls of the sampling system. The diffusion coefficient of a particle varies inversely with particle size with smaller particles diffusing more quickly than larger particles. Loss of particles by diffusion to the walls is much faster in highly turbulent flows which have thin boundary layers, and consequently, high mass transfer coefficients (Kittelson, 1990). Diffusion is most important for particles smaller than about 0.05 µm in diameter. Diffusional losses for a representative diesel exhaust aerosol were calculated (Kittelson, 1990) based on turbulent mass transfer to a pipe. Diffusional losses for 0.03 µm and 0.30 µm were found to be less than 0.2%. Diffusional deposition losses can be minimised by using high flow rates and short sample lines.

5.2.1.4. Inertial Impaction

Inertial impaction arises from the inability of particles to follow gas streamlines as a result of the particle inertia, and is therefore a product of particle mass and velocity. Non-isokinetic sampling errors and particle deposition in bends and contractions will affect the indicated particle measurements. However, the magnitude of these effects is generally small for particles in the sub-micrometer diameter range characteristic of particle emissions, although there is scope to lose significant mass from the larger particles present in the 1-3 µm range. It was noted by Dickens *et al*, 1997 that particles larger than 2.5 µm are generally not sampled in the current regulated mass emissions regime, where a ‘hat’ is placed at the sampling point. Inertial impaction losses may be minimised by avoiding sharp changes in sample line direction or diameter.

5.2.1.5. Electrostatic Deposition

Electrostatic deposition can occur in sampling systems where sample transfer lines are made of a material that can be electrically charged. Particles from vehicle emissions are naturally charged as a result of the combustion process. If a sample line carrying the diesel particles is charged, the resulting electric field will drive a portion of the charged diesel particles to the walls where they will be removed from the gas stream. This process is more significant for larger soot particles (Johnson, 1993). Electrostatic deposition losses may be minimised by the use of metal sample lines to avoid electrostatic build-up and avoiding PTFE sample lines which in contrast are prone to charging.

5.2.2. Aerosol ageing processes

The main gas to particle processes taking place during dilution were described in chapter 4, including nucleation, condensation, and adsorption. Nucleation and condensation effects have been frequently encountered during sampling of exhaust aerosol (Frisch et al., 1979, MacDonald et al. 80) at moderate dilution ratios. Adsorption is considered as the main mechanism by which particles obtain their soluble fraction (Reichel et al., 1983). Hydrocarbons and sulphates adsorbed on the solid deposits of the exhaust line and the dilution tunnel can later be desorbed (outgassed), e.g. due to temperature increase in those regions. Since the prediction of outgassing is difficult, desorption may lead to random peaks in the particle concentration due to nucleation of the desorbed components in subsequent regions of lower temperature (Graskow et al., 1998).

Agglomeration was already described in chapter 4. The process is favored by high temperatures and particle concentration. It can be significant when the the particle concentration is still quite high, i.e. in the sampling lines before before dilution. Table 5-1 summarises these processes and their impact to aerosol properties.

Table 5-1: Particle Dynamics and Transformations (Kittelson to EPA, 1999)

Process	Impact
Particle coagulation	1. Dependent on particle size and concentration 2. Does not affect total particle mass 3. Causes decrease in particle number concentration and increase in particle size 4. Increase in particle size may affect loss mechanisms 5. May affect diesel aerosols if dilution is delayed, not critical after typical diesel exhaust dilutions 6. Typical time constant, $T = l/kN_0 - 10^9/N_0$ (s) for diesel size particles, N_0 = initial particle concentration (I/cm^3) (Fuchs,1964)
Adsorption / desorption	1. Adsorption / desorption of volatile components will affect size and mass of measured particulate matter 2. Availability of particulate surface will affect degree of adsorption / desorption 3. Driven by saturation ratio
Nucleation	4. Homogeneous nucleation may create large numbers of new particles 5. Nucleation rates are highly nonlinear functions of saturation ratio 6. Heterogeneous nucleation leads to the growth of existing particles
Condensation/ evaporation	7. Condensation / evaporation of volatile constituents will affect size and mass of measured particulate matter 8. Affected by saturation ratio, testing conditions such as: temperature, pressure, humidity 9. Particles formed by nucleation may grow by condensation

5.3. Sampling and transfer line

Starting with the sample extraction from the exhaust gas flow, a good practice is to try to achieve isoaxial and isokinetic flow through the extraction probe. Sampling is considered isoaxial when the streamlines in the sampling probe are parallel to the streamlines of the free exhaust gas flow. Sampling is considered isokinetic when the flow velocity in the sampling probe is equal to the velocity of the free exhaust gas flow. More details on those two definitions may be found in relevant literature (Hinds, 1982; Willeke and Baron, 1993). Both these requirements are usually set for particle sampling in order to avoid impaction losses of particles in the sample point. They are considered significant only when sampling super-micrometer particles where the particle inertia is large enough for particles to miss the streamlines and escape sampling.

Ahlvik et al. (1998) developed a simplified model to calculate aspiration efficiency. Ntziachristos and Samaras (2000a) applied this model to estimate the losses associated with tailpipe sampling over a transient cycle when probe diameter was selected for isokinetic sampling under moderate engine operation. Figure 5-1 shows the results of this calculation. Although deviation from isokinetic is indeed insignificant for number concentration overall during the cycle (only ~4% higher number recorded at maximum deviation), it can still be important for volume concentration because it mainly relates to large particles (~25% higher volume concentration recorded at maximum deviation).

As a conclusion, measures to achieve isoaxial and isokinetic sampling should be foreseen for moderate engine operation in order to exclude any concentration under/over- estimation, at least for steady stage engine operation. During transients, some sampling deviations from true concentration will be inevitable but should rather be considered moderate, compared to the effects e.g. of the dilution realisation. A solution to this is to apply some theoretical model to correct for aspiration efficiency effects.

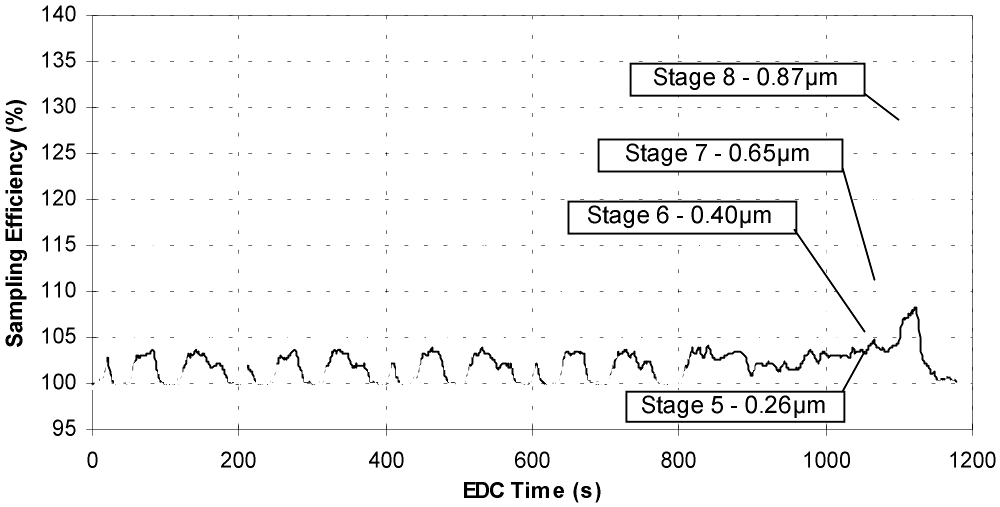


Figure 5-1*:* Sampling efficiency over a transient cycle (Ntziachristos and Samaras, 2000a).

A second requirement from the sampling system is to provide a fast as possible transfer of the sample from the vehicle to the instrumentation. Residence of a particle laden sample to the transfer lines for a long time is a source of particle loss on the walls of the piping and increases the probability of particle-to-particle and gas-to-particle interactions (coagulation, condensation, adsorption, etc.). A description of the main loss mechanisms follows in the next section. The collective effect of those processes is that aerosol characteristics start to deviate from the before sampling conditions and the deviation is stronger as residence time increases. On the other hand, a minimum residence time needs to be retained – especially in mixing chambers – in order to achieve a homogeneous sample at the outlet of each device.

It is difficult to assess a priori what is the optimum residence time for each sampling system since this depends on a number of parameters such as the number of devices intervening between the aerosol source and the instrumentation, the aims of the measurement and the space configuration of each facility. A recent questionnaire including information from several labs (Kittelson, 1999) showed that the residence time in the sampling system varies from 15 ms to 4 s. In order to eliminate secondary phenomena, it should probably be advisable to limit the residence time in the milliseconds region. In any case, each relevant investigation needs to accurately report the sample residence time in the various components of the system in order to improve comparability or explain variations with corresponding studies.

Several secondary phenomena, such as adsorption or particle loss due to temperature gradients can be eliminated by thermally insulating or even heating the sampling lines. This is lately a common practice (Abdul-Khalek et al., 1999; Ntziachristos and Samaras, 2000b)in order to bring the conditions of the exhaust aerosol before the instrumentation as close as the conditions encountered at the tailpipe. Heating is more important before the primary dilution stage where volatile species concentration and adsorption / condensation potential is maximum. Insulation or heating of the sampling lines also decreases any negative thermal gradients from the flow to the transportation boundary walls. This is a positive side-effect because it increases the homogeneity of the mixture and also eliminates the losses of the particles due to their thermal motion towards the wall (thermophoresis). In general, it is advisable to avoid significant thermal gradients between the sample and its boundary walls which may provide the source of significant losses and aerosol variations.

A sampling and transfer system need also to take consideration of the flow conditions within the transfer lines. Usually turbulent flow is a better choice because it enhances the mixing of the particles with the transport in the sampling lines and improved homogeneity. Also turbulent flow is mainly associated with higher flow velocities and hence shorter residence times. However, turbulence formed by abrupt contractions or expansions of the cross sections should be avoided because such conditions are usually associated with significant particle deposition in the neighbouring walls and hence particle loss.

In order to preserve the operability of a sampling and transfer system, one needs to consider the importance of regular cleaning. The sampling system needs to be easy to dismantle and all components easy to visually inspect and clean. This also includes any ejectors or orifices utilised. Cleaning is important first to make sure that flow conditions do not vary from the design and secondly to exclude any artefacts originating from wall outgassing of particle re-entrainment. Both these phenomena have been observed in laboratory conditions (e.g. Kittelson et al., 1991, Hall and Dickens, 2000). The former is responsible for an increase of the measurement variability due to spontaneous condensation of species in the transfer lines and the latter for the artificial emission of very coarse particles which originate from agglomerates re-entrainment of the sampling walls. Although for mass measurements such effects are not very significant because some kind of mass equilibrium starts to develop after some point between mass deposition and mass re-entrainment, for particle number characterisation this is unacceptable because it may provide significant complications in the interpretation of variability.

5.4. Dilution

5.4.1. Aims of the dilution process

The most significant process of the exhaust aerosol handling is the dilution process. Dilution is necessary because the instruments usually applied for exhaust aerosol measurements are capable to record much lower particle concentrations than one meets at vehicle exhaust. Therefore, limits for the dilution ratio – i.e. the mass of diluted mixture produced per unit mass of exhaust sample – may originate from the specifications of the instruments applied. Instrument maximum range defines the low dilution ratio limit and instrument sensitivity the high limit. Furthermore, additional factors imposing dilution include the high exhaust gas temperature and water content which - if left at their tailpipe values –may both affect the measurement and damage the instruments.

However, even if such difficulties are not relevant to a particular measurement, dilution would still be necessary if the aim of the exhaust gas characterisation is to analyse a sample which - if possible – is close to the actual emissions of aerosol in the atmosphere. This is a particularly demanding target since the ageing of the exhaust gas in the atmosphere is difficult to predict and simulate, because it depends on the actual ambient conditions (temperature, humidity, wind conditions, existing particle species in the atmosphere, etc.) and traffic conditions (urban congestion, highway driving, etc.).

Additionally, when trying to simulate atmospheric dilution one needs to also take into account the time dimension since the ageing of the aerosol in the atmosphere is a dynamic process starting immediately after emission and leading to the removal of the particle from the atmosphere. Hence, the properties of the exhaust aerosol in the atmosphere are a function of time and are affected by physical mechanisms (gas-to-particle and particle-to-particle interactions) and chemical transformations (photolysis, ozonolysis, reactions with gaseous species, etc.) (EPA Health Draft 2000– to become citable soon).

Atmospheric dilution is a fast process. What is generally accepted for dilution at free-flow driving is a time constant of about 1 s to reach dilution ratios over 1000 with milliseconds residence time in moderate dilution ratios (<100) (Kittelson et al., 1999). On the other hand, laboratory dilution processes involve longer stabilisation times at moderate dilution (especially when measurements are conducted via a CVS system – see Chapter 5.5.).

However, there are a number of parameters associated with laboratory dilution which can and need to be controlled to try to approach atmospheric dilution. Before looking at the parameters to control during dilution, a description of the main physical processes encountered after particle sampling are discussed in the following section.

5.4.2. Determination of the dilution process

The extent of the aerosol ageing mechanisms discussed previously largely depends on the details of the dilution process. This is because the concentration of the different species, the temperature of the exhaust gas, the final humidity, etc. are all a function of the dilution process (and the exhaust gas stream properties). Therefore, by adjusting the dilution process variables one may produce aerosol of different specifications by enhancing or suppressing any of the before mentioned mechanisms.

There are four main variables affecting the impact of dilution on the aerosol properties, namely dilution ratio, temperature, dilution air humidity and residence time at dilute conditions before sampling. Other variables associated with dilution effect on emissions include the type of dilution system and geometry, background particle concentration etc., but their effects either are difficult to quantify or they can be removed relatively easy (e.g. by filtering the dilution air).

Kittelson et al. (1999 report to EPA) thoroughly summarise the experience collected by several investigations, related to the effect of dilution on the aerosol specifications. This experience need not be repeated here. The main conclusions drawn from this review are:

- dilution ratios in the critical range of 5 to 50 may promote the formation of a nanoparticle mode as particles nucleate as the exhaust is cooled,
- the role of relative humidity in dilution air is not fully understood
- the lack of carbonaceous material surface area in modern diesel engines for adsorption of volatile compounds may allow saturation ratios to become high enough to favor nucleation and the creation of a large nanoparticle number mode,
- non-carbonaceous material in the exhaust such as metals or sulfuric acid may act as nucleation sites for heterogeneous nucleation of volatiles, even in the presence of carbonaceous material,
- temperature residence time in the critical dilution ratio range can markedly affect the production of nanoparticles.

Since then, a number of additional studies were conducted which provide more light in the effects of dilution parameters on the aerosol characteristics. The main conclusions of these studies follow.

Shi and Harrison (1999) examined the potential of ultrafine particle formation from sulphate nucleation as a function of dilution ratio, humidity and temperature by studying the emissions of a heavy duty engine. They found that the number concentration of particles recorded primarily depends on the first stage dilution ratio with increasing – but moderate - ratios generally leading to the formation of ultrafine particles. They also calculated that temperature decrease and relative humidity increase results in higher sulphate mass of ultrafine particles, which, according to the authors, is consistent with the mechanisms of binary H_2O – H_2SO_4 homogenous nucleation. However calculated rates are much smaller than experimental results would have required. The authors attribute this deviation to parallel homogeneous nucleation of organic and inorganic species and also heterogeneous nucleation of sulphates.

Graskow et al. (2000) examined the particle emissions of a direct-injection spark-ignition engine with two different dilution systems. The first system (free mixing) is a two stage dilutor with primary dilution ratio of 550 and residence time of 100 ms and a secondary dilution of 11.8. The second system (forced mixing) employs a primary dilution ratio of 15 and secondary of 25 with an inter-stage residence time of 1 s. Due to the large differences between the two systems, the authors observed that free mixing results in a shift of the particle size distribution towards smaller particles than forced dilution, although the difference in the absolute number concentration was not much different between the two cases. They attributed this difference to the long residence time of the diluted aerosol in the inter-stage region of the forced mixing system and at moderate dilution ratio. Those conditions favour the agglomeration of nanoparticles and the condensation of volatiles onto existing nuclei. This is believed to reduce the number and increase the size of the aerosol particles.

Finally, Abdul-Khalek et al. (1999) conducted a parametric study of the effect of the main four dilution variables on the exhaust aerosol of a heavy duty diesel engine. The authors utilised a two-stage dilution system to sample raw engine exhaust. They varied the primary dilution ratio from 12 – 40, the residence time after first dilution in the range of 100 – 1000 ms, the diluted mixture relative humidity from 15 – 40% and the primary dilution temperature from 13 – 65°C. The main conclusions drawn is that mostly a bimodal distribution was reached with only the nuclei mode affected by dilution conditions. The nuclei mode variation was 1.5 orders of magnitude within the range of variables examined for constant relative humidity while relative humidity increase from 15% to 40% increased the number concentration of nuclei particles by 30%. The authors attributed such effects to the nucleation of sulphates and their subsequent growth by condensation of sulphuric acid, water and hydrocarbon species.

The outcome of the studies conducted over the last decades is more or less well perceived and converges to the following observation: The agglomeration particle mode, which mainly contributes to particle mass emissions, is generally insensitive to dilution conditions and mainly depends on the engine (vehicle) / fuel specifications. On the other hand, the existence or not of a nuclei mode, as well as its properties, are a strong function of the vehicle, fuel and sampling (i.e. mainly dilution) variables.

However, late evidence shows that particles in the nucleation mode are encountered under atmospheric dilution conditions (Shi et al., 1999, Kittelson and Watts, 2000, Kittelson et al., 2000). If this is the case, then it would be advisable to select those dilution conditions which may potentially result in the formation of the nuclei mode. Again, since this is a rather obscure definition of sampling conditions, some safe measures which may be taken to avoid unrealistic results would include short residence times in moderate dilution ratio and control of the dilution temperature and relative humidity to avoid extremes in the nuclei mode concentration.

5.5. Current status: Review, CVS problems

5.5.1. CVS Principles

Current legislation in European Union (Directive 98/69/EC) defines that particulate matter (PM) sampling should be conducted via a Constant Volume Sampling (CVS) system. Initially, the CVS system for particulate matter sampling from diesel vehicles was introduced in Europe by directive 88/436/EEC. However, the first application of CVS techniques dates back to late 1950s for gaseous pollutant characterisation from gasoline vehicles (SAE Recommended Practice J1094a). The concept introduced with the CVS system is the homogeneous mixing of exhaust flow with fresh air prior to sampling. This is necessary to freeze reactions between the species in exhaust, to decrease the concentration of pollutants to a measurable range and to mimic atmospheric dilution. The effectiveness in achieving these targets will be commented below.

Aim of the CVS system is to achieve a constant volumetric flow of exhaust gas, regardless of engine or vehicle operating condition, in order to simplify the sampling process. In that respect, the tailpipe exhaust flow is diluted with filtered air in a dilution tunnel prior to sampling. The constant volumetric flow is achieved with the use of a positive displacement pump (PDP-CVS) or a critical flow venturi (CFV-CVS) and a pump at the outlet of the dilution tunnel. The latter requires the use of a heat exchanger to bring the diluted exhaust gas flow at a constant temperature before the venturi. However, an alternative is not to use a heat exchanger but to monitor the diluted gas temperature before the venturi and from that to deduce the (variable) volumetric flow during the measurement. Legislation defines the details of the dilution tunnel configuration; the most important being a ReD>4000 and a minimum internal tunnel diameter of 200 mm.

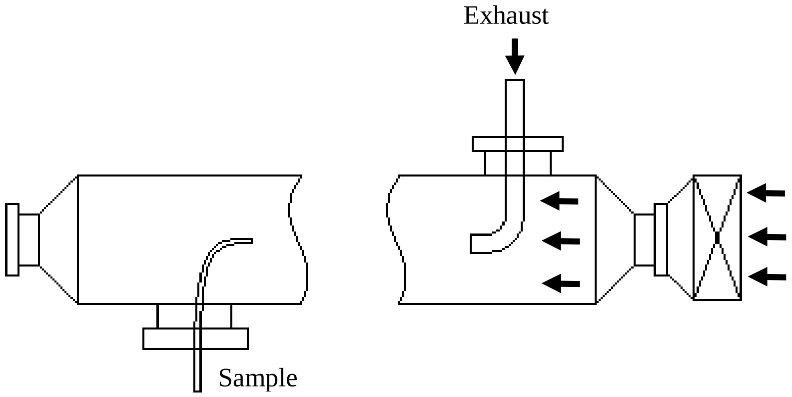


Figure 5-2*:* Schematics of CVS dilution tube

PM samples are extracted from the dilution tunnel with a sampling probe which is installed several diameters downstream of the raw exhaust / dilution air mixing point in order to draw sufficiently mixed aerosol sample. The sample flow is maintained proportional to the total flow in the dilution tunnel by a sampling pump. The sample flows through a filter, which collects the suspended particles. According to legislation the temperature at the filter position should not exceed 52°C. In some installations, two cascade filters are used to decrease the possibility of escaping particles. Also, in order to achieve this relatively low temperature, a secondary dilution prior to the filter holder may be required, especially in the case of heavy duty engines. The total mass of particles emitted by the vehicle or engine examined is calculated by weighing the mass of particles collected on the filter(s) and inferring the results to the total flow in the dilution tunnel.

5.5.2. CVS Implications for particle mass measurements

CVS systems have historically proved to be a satisfactory baseline sampling condition for particle mass measurements by providing a constant exhaust flow and a common temperature range of sampling. The constant exhaust flow may further provide not only an isoaxial, but also isokinetic sample extraction. The latter, although generally not considered a prerequisite for accurate submicron particle sampling, it may still be necessary to accurately proportionate those coarser particles which significantly contribute to the mass measurements (Ntziachristos and Samaras, 2000a). Finally, dilution of the exhaust samples decreases the humidity of the flow, which may significantly soak the filter and may plug the sampling probes.

Several values may vary in different CVS installations, including flowrate, residence time and dilution ratio achieved. However, those sampling parameters do not fall on the focus of the legislation, which only defines the maximum temperature at the sampling position. Experience has shown that the magnitude of those variables may have an effect on the mass collected. More specifically, the effects of the dilution ratio on the particle mass collected, even independent of the temperature in the dilution tunnel, have been analysed in the 1980s by several investigators (McDonald et al., 1980, Plee and McDonald, 1980, Reichel et al., 1979). A summary of these investigations is provided by Ahlvik et al. (1998). The main conclusion of those studies is that even when keeping the temperature constant, a reduction of the dilution ratio increases the particle matter collected. The increase of the mass is associated with the higher concentration of volatile species and the subsequent enhancement of the condensation and absorption / adsorption processes as dilution decreases. Additionally, low dilution increases the fuel sulphur to sulphate conversion and subsequently the mass collected on the filter (Frisch et al., 1979). Hence, the mass quantity collected on the filter also depends on the particularities of the CVS used.

Lately – and in view of the continuously improving engine (soot) emissions – several other challenges associated with CVS mass collection have been raised. Clark (2000) has provided a good summary of those. In short, questions arising for accurate PM measurement from a CVS include the range of dilution ratios to employ since on one hand low dilution ratios are necessary to collect sufficient mass and on the other, high dilution ratios not to exceed the sampling temperature. Secondly, the cleanliness of the dilution air is important since the filter may also collect background solid cores, which – if significant in quantity – may also lead to error estimates of emissions. However, since such cores act also as condensation sites for volatile species, they should not be totally removed not to underestimate the contribution of the volatile fraction in the total PM. Finally, dilution tunnel walls may act as a hydrocarbon pool, spontaneously adsorbing and outgassing hydrocarbon species. The effect of wall hang-up leads to variable results according to dilution tunnel history and condition during the measurement.

5.5.3. CVS Implications for physical characterising the particles

All variables affecting the total mass of particles collected from CVS measurements (adsorption / absorption and nucleation) naturally affect all other particle characteristics (number concentration, size distribution, chemical speciation, etc.). Presumably, even more significantly so, since large differences e.g. in the number concentration of ultrafine particles resulting from the CVS particularities is only little reflected to mass measurements, because of the small size of ultrafine particles. Additionally, when size distribution is considered, the effect of coagulation is important.

A significant number of investigations has been focused on the effects of the CVS details on the number concentration and size distribution of emitted particles. In principle, it is generally considered that CVS systems leave exhaust aerosol at moderate dilution ratios (3 : 1 to 30 : 1) more than it takes for the exhaust plume to pass from tailpipe conditions to very high atmospheric dilutions. According to Kittelson (Kittelson et al., 1999) a DR of 1000 : 1 may be reached within 1 s at highway driving, while the same study showed that in most laboratories it takes more than 1 s to dilute the sample at a DR of 10 : 1 or lower. This deviation of the CVS dilution from the ‘actual’ process is believed to bring the nucleation of volatile species to unrealistically high levels. This is not to say that ultrafine particles do not exist in the atmosphere from various sources; roadway ambient studies have shown this (e.g. Harrison, 2000). However, very high values of nuclei particles when sampling at moderate dilution ratios (e.g. Bagley et al., 1996) might provide difficulties to compare results obtained at more realistic, higher dilution ratios (Kittelson, 1998). In that respect, CVS measurements without reporting the particularities of each configuration may bring complications in evaluating any results.

However, as has been shown in the previous section, there seems to be a DR limit above which aerosol characteristics are less sensitive to dilution ratio changes. Even with the least demanding requirements (Kayes et al, 1998) this range is located beyond the value of 15 : 1 while others (Abdul-Khalek et al., 1999) locate this limit at 40 : 1. In any case, such high dilution ratios are difficult to reach with full-flow CVS systems even for light duty vehicles because of the significant pumping requirements involved. In that case, as explained before, aerosol characteristics are a significant function of the CVS particularities.

With regard to particle number concentration and size distribution, an additional nuisance parameter relates to the possible coagulation of particles, especially if the exhaust flow has to travel for long at tailpipe concentration before it reaches the dilution tunnel. Maricq et al. (1999) have shown that coagulation of diesel aerosol samples results in a significant shift of the accumulation mode to larger sizes. Although coagulation can also take place within the vehicle exhaust line, it is in the dilution process that coagulation depends on non-vehicle parameters and hence need to be minimised; also having in mind that atmospheric dilution generally results in rapid high dilutions which suppress coagulation.

5.5.4. Uncertainties related with CVS sampling

In an effort to evaluate the CVS capability of providing representative and reliable samples of exhaust particle emissions, one comes to confronting experiences. Evidence collected in the framework of CVS experimental studies show that depending on the emission source, engine operation considered and CVS particularities, measurements can either be reasonable repeatable or totally unrealistic of tailpipe conditions. A brief summary of those studies is given in the following paragraphs.

A DG XI sponsored study conducted by AEA Technology (1999) examined the particle emissions of a Euro II diesel vehicle where sampling was carried out via a conventional PDP-CVS system providing DRs up to 30 : 1. The study recommended that a straightforward use of the CVS system in its standard mode can be used without the addition of extra equipment. Additionally, an investigation sponsored by ACEA and carried out by FEV Motorentechnik and University of Duisburg suggested that the variation of emissions from a Diesel vehicle conducted from a CFV-CVS is very low for the whole measurement campaign (however, particles concentration in the <20 nm size range differed by more than an order of magnitude between measurements). A study evaluating the potential of CVS for gasoline PM measurement (Kayes and Hochgreb, 1998) found that the uncertainty added to the particle concentration by the dilution process is undetectably small. This is on a per day basis; on a day-to-day scale, the authors found that the variability may exceed an order of magnitude difference from the average.

On the other hand, several other investigations point out potential complications with CVS measurements. A recent common DETR/SMMT/CONCAWE research programme (Andersson et al., 2000, Wedekind et al., 2000) examined the aerosol characteristics from 4 HDV engines sampled via a PDP-CVS system. The study concludes that CVS measurements are deemed to be appropriate for the determination of the accumulation mode distributions. However, there is a greater uncertainty with the nanoparticle mode (especially for steady-state tests) because of the long stabilisation times required by the CVS when shifting between driving modes. However, the same tendency was found when a partial dilution system was employed for HDV measurements (Abdul-Khalek et al., 1998) with a residence time in dilute conditions in the order of 0,5s.

In the case of gasoline vehicles testing, several measurement artefacts have been observed when conducting CVS measurements affecting, both the representativity and the repeatability of measurements. Analytical studies aiming at explaining the source of ultrafine particles in gasoline vehicles (Maricq et al., 1999, Hall and Dickens, 2000) have identified the components of the CVS and transfer line as a significant source, rather than the vehicle itself. They attributed such effects to outgassing or pyrolysis of components collected on the sampling walls. Similar views have been expressed by Kittelson and Johnson (1991) where particle reentrainment and outgassing from the exhaust transfer line from the vehicle to the dilution tunnel is considered as a source of variability. Finally, Kayes and Hochgreb (1998) report that the cleanliness of the tunnel is important for the extent of particle condensation and hence the condition of the tunnel plays a role on the measured concentration.

There is another dimension of variability when measurements are conducted in different facilities equipped with CVS systems. This relates to the sensitivity of the nanoparticle mode to sampling parameters (mainly DR, residence time, sampling temperature) as described in the previous section. Therefore, for CVS systems and transfer lines considerably differing in their operation parameters or design variables, one should expect variable results even when emissions are produced from the same source. This downgrades the comparability of results obtained in different facilities.

Kittelson et al. (1999) provide a list with recommendations to enhance the confidence on particle samples analysis (also included in a relevant DG III study (2000)). However, some of the recommendations are difficult – if no impossible - to apply to existing CVS systems. As an example, the list recommends that the temperature and residence time should be carefully controlled in the dilution ration range 5 – 50 : 1. However, both temperature and residence time in an existing CVS system are a function of dilution ratio and those two cannot be controlled independently at wish. Additionally, it is suggested that the engine to tunnel lines should be similar in temperature to exhaust pipe. Although this is not impossible, it is associated with a high cost when the whole exhaust gas temperature needs to be maintained at tailpipe temperature prior to entering the dilution tunnel.

As a conclusion, existing experience is diverse on whether CVS measurements can provide repeatable results of particle emission characteristics and representative samples of real-world emissions. Specific recommendations to improve repeatability might prove costly for already built CVS systems. Furthermore, even if particular measures are taken to resolve the repeatability issue, the problem of variable sampling conditions between different installations remains, thus hindering comparability of results collected from different sources.

5.6. Alternative sampling and dilution systems

5.6.1. Partial flow dilutors

This contains systems where only a fraction of the total exhaust flow is sampled and diluted. Partial flow diluters have been extensively used previously in combustion studies to measure high concentration and high temperature aerosols (see for example Biswas, 1993). The main advantage of partial flow diluters is that conditions during sampling are much easier to control than with full flow diluters. There are many different types of partial flow diluters but they all share some characteristics. The dilution ratio is usually adjustable and is not dependable on the amount of exhaust gas. With partial flow diluters, full control of temperatures and relative humidity can be realised. Residence time in the diluter can be adjusted. Total emissions can not be derived directly. To determine total emissions also the amount of exhaust gas has to be measured. Because only partial sample is taken, sample might also not be homogenous. Variable flow rates and pressures in the sampling point complicate sampling and isokinetic sampling in some constructions is difficult to achieve. Differences between dilution tunnel and partial flow diluters are summarised in table 5-2

Table 5-2: Differences between dilution systems.

DILUTION TUNNEL (FULL DILUTION)	**MINI DILUTOR (RAW EXHAUST)**
Advantages: • Constant flow/pressure-control of temperature • Labs already have it • Homogeneous mixing exhaust/air • Sampling of particulates comparable to PM • May simulate atmospheric dilution? • Calculations #/s, #/km straightforward	**Advantages:** • Full control of T, RH, DR possible • Minimum losses of particles • Low (zero) background HC, particle concentration possible • Residence time may be adjusted • Full similarity between different labs may be achieved • May simulate atmospheric dilution?
Disadvantages: • Uncontrolled volatile condensation • High residence time in partial dilution • Limited control of DR / humidity / temperature • Relatively high background particle / HC concentration • Re-entrainment / outgassing • Some labs clean the tunnel for gasoline / diesel, some use different tunnels, some use PM equilibrium concept	**Disadvantages:** • Not homogenized sample drawn from exhaust • Pressure fluctuation, condensation of water in the sampling line many cause errors • Far from isokinetic sampling may provide errors • Calculations #/s, #/km require additional determination of exhaust flow • PM / particle samples drawn from different locations

5.6.1.1. Mini Dilution Tunnel

Structure comparable to CVS, only difference is that whole exhaust gas is not diluted. A small amount of gas is drawn into a small dilution tunnel and dilution ratio is scaled by adjusting the ratio between the dilution air and air drawn from tunnel. Supplement air is drawn from exhaust for dilution.

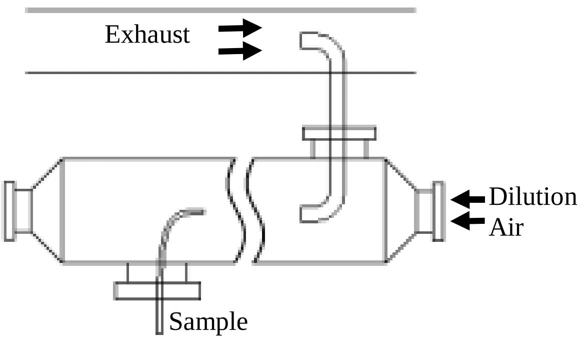


Figure 5-3: Mini dilution tunnel

These systems have smaller dimensions compared to CVS. They also provide constant dilution ratio, even in transient cycles, by adjusting the flows continuously. The need of continuously adjusting the massflow meter could be considered as a disadvantage. Another con compared to CVS is the need to measure total exhaust flow to get the total emission. Total flow measurement is difficult in transient cycles due to rapid changes in exhaust gas volume.

Effect to particles

In mini dilution tunnel the result of dilution is easier to adjust than in CVS because of the smaller flowrate. Pure soot and nucleation particles are possible to achieve if desired, with proper settings of dilution air.

5.6.1.2. Ejector Type Diluter

In ejector type diluter, sample is drawn in the diluter by the under pressure generated with the annular nozzle where the pressure is decreased by increasing the speed of the dilution gas flow. The generated under pressure draws in a sample that is proportional to the under pressure generated. The under pressure is proportional to the dilution gas flow rate i.e volume. By adjusting the dilution gas flow one can adjust the sample drawn in the diluter, keeping the dilution ratio constant at the same time.

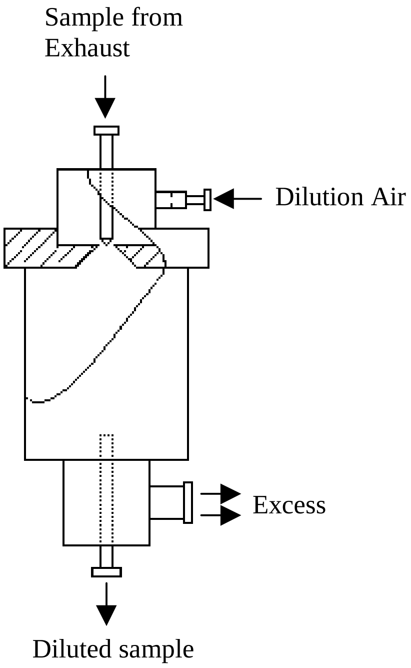


Figure 5-4*:* Ejector type diluter

Ejector type diluter keeps constant dilution ratio. Dilution ratio can be scaled by cascading diluters. Dilution ratio originates from the dimensions of the diluter (Koch et al., 1988). Small size is advantage if doing measurements in a non-permanent measurement site. When measuring high concentrations material can accumulate in the sampling nozzle. This can gradually block the nozzle. This accumulation is due to small size and cooling of the nozzle. To prevent condensation effects and blocking of the nozzle, high temperature dilution air can be used. Instrument is also sensitive to the pressure difference between the dilution chamber and inlet.

Effect to particles

Ejector type diluters are usually so small that the residence time is small and the flow is turbulent inside the chamber. This results in rapid mixing and only small changes in particle characteristics can occur. Cold air dilution may result in condensation on the chamber walls and on particles. Elevating the temperature of the dilution air prohibits condensation and nucleation. With temperatures that prevent condensation and nucleation pure soot particles can be obtained. Nucleation mode particles are difficult to get because the blocking of the nozzle prohibits the use of cold air for dilution.

5.6.1.3. Rotating Disk Diluter

In rotating disk diluters dilution is done by transferring small amounts of sample gas into the dilution gas. The transferring is done with rotating disk what has small caves in it. These caves are filled with exhaust gas in the other line and are then transferred to dilution gas line. The dilution ratio is scalable by adjusting the rotating speed of the disk or changing the number of caves in the disk. Rotating disk diluter is a part of NanoMet system (Kasper et al., 2000).

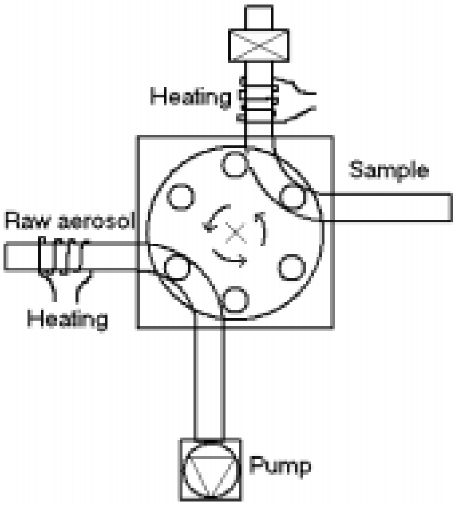


Figure 5-5*:* Rotating disk diluter

Due to little experience of this type dilutor much of practical pros and cons is not known. Advantage of this diluter is fast and easy adjustment of dilution ratio by changing the rotating speed of the disk. Disadvantage is the requirements for small pressure difference between the two sampling lines and dilution line and environment (Hueglin et al., 1997).

Effect to particles

The capability to use hot and cold dilution air allows to set operating point and effects to particles as wanted. Pure soot and nucleation particles are possible to achieve if desired, with proper settings of dilution air.

5.6.1.4. Aspirated sampling probe

In this method sample is extracted from the exhaust flow and diluted simultaneously. The method has been applied earlier for combustion studies (e.g. Biswas, 1993). The sample is diluted by introducing the cooled dilution air in the tip of the probe through aspirated tube (fig. 5-6).

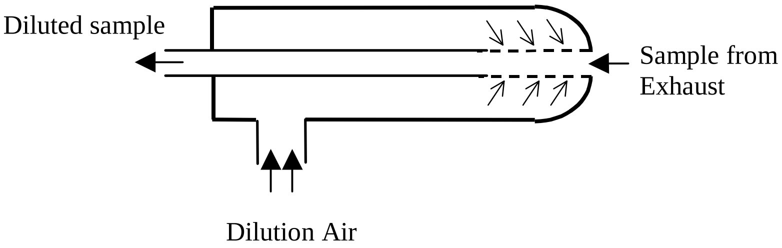


Figure 5-6: Aspirated sampling probe.

Dilution ratio can be controlled by adjusting dilution air flow and measuring the flow exiting the diluter. This construction provides high mixing rate and minimises thermophoretic losses.

Effect to particles

The capability to control dilution air temperature allows to set operating point and effects to particles as wanted. Pure soot and nucleation particles are possible to achieve if desired, with proper settings of dilution air.

5.6.1.5. Capillary Diluter

In capillary diluter sample flow is divided into two parts. One part goes straight through and the other part is filtered. Dilution ratio can be controlled by adjusting these two flows.

In this construction the dilution ratio can be easily controlled and determined. If total flow is known only the ratio of flows is needed. Disadvantage is the use of filtered gas for dilution. Filtration can leave gaseous components intact and this can cause nucleation or condensation later in the sampling line and makes the measurement of gaseous emissions difficult. Dilution ratio is dependent on particle size and this might be disadvantage or requires calibration of the dilution ratio as function of particle diameter.

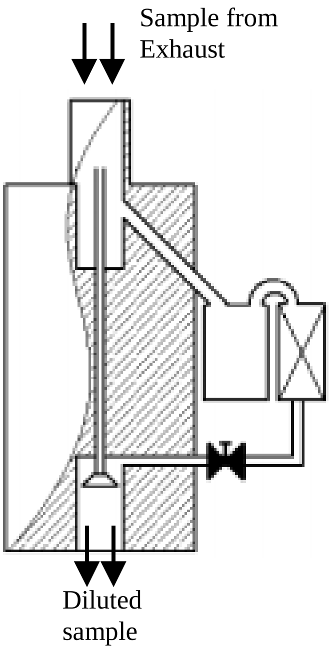


Figure 5-7: Capillary diluter

Effect to particles

Capillary diluter itself doesn’t change particle properties at all if the temperature stays constant in diluter. However for most instruments the temperature has to be lower than at the exhaust so some way to reduce temperature has to be utilised. This will lead to difficulties due to condensation. Gaseous components are not diluted at all. This can also be a disadvantage. The dilution ratio is a function of particle diameter and therefore particle distributions change in capillary diluter.

5.6.2. Alternatives or additives to dilution

These systems are not diluters, but they can be used in sample conditioning in addition to dilution.

5.6.2.1. Thermodenuder

Denuders have been used for a long time, mainly in atmospheric studies, to selectively remove specific species from a gas flow. The denuder removes gas-phase organics by diffusion to adsorbent surface like activated charcoal or polymere resins (Turpin et al., 2000). The adsorbent can be chemically analysed after each measurement to obtain information on the species removed (Poon et al., 1993).

The adsorbent surface usually forms a cylinder wall where gas flow passes by with specific species diffusing on the wall while the remaining flow exits the device. An alternative of a denuder device is the thermo-denuder where the exhaust gas flow is heated up to certain temperature and any condensed volatile material (mainly organics and sulphates) is evaporated before it is removed from the gas phase by diffusion in the adsorbent wall (fig. 5-8.). This device has been used in the past to separate the volatile from solid particles (Mayer, 1996).

The efficiency of a specific device to strip the solid phase depends on a number of parameters such as the residence time of the exhaust flow in the denuder, the adsorbent active surface per volume unit of exhaust flow, the adsorbent material etc. Also, since the adsorbent material may become saturated it needs to be changed often to preserve its adsorbing properties.

Effect to particles

It practice, it is required that the denuder has maximum efficiency in removing gaseous species and minimal losses of particles. However, a certain fraction of very small particles will be lost in the denuder by diffusion and thermophoresis increasing the losses of the sampling system. Another side-effect is that the thermal treatment of particles to remove any condensable layer may result in changes on their structure during volatiles evaporation (Kütz et al., 1992).

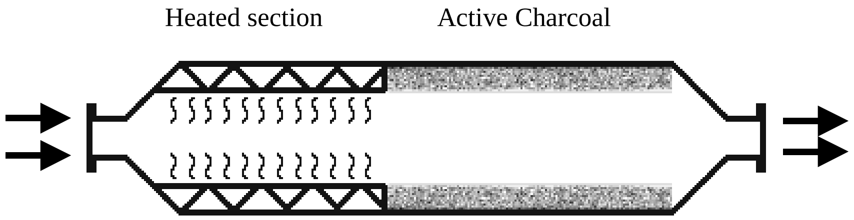


Figure 5-8: Thermodenuder

5.7. How to sample

5.7.1. General guidelines

Regardless of sample conditioning and setup following general guidelines should be followed as closely as possible.

Sampling:

- as close to isokinetic as possible
- minimised sampling line length to reduce losses
- minimised heat transfer in sampling line to reduce losses and avoid condensation and/or outgassing
- conducting material in sampling lines to reduce electrostatic losses

Dilution:

- filtered to remove background particles from dilution air
- controlled temperature of dilution air
- controlled humidity of dilution air
- controlled residence time
- minimised residence time after final dilution

5.7.2. Sample conditioning

In laboratory, all conditional parameters can be stable and constant. Only problem is that it is difficult to decide what these parameters should be. With different parameters one can decide what kind of processes occur within dilution and even obtain results that are desirable. Dilution on the road depends on conditions such as the speed of the vehicle, aerodynamics around the exhaust pipe and properties of the surrounding atmosphere such as temperature and humidity. Defining normal atmospheric conditions is impossible due to different climate parameters around the world. Factors affecting dilution results are e.g. temperature, composition and rate of mixing. Due to these parameters one can obtain different kind of number distributions depending on the climate where the dilution takes place. Dilution ratio is high on highway conditions but low in slow traffic like traffic jams. According to roadside measurements dilution ratio can rise up to 100 in half a second and up to 1000 in a second (Kittelson et al., 1999).

Sampling and dilution conditions can be chosen based on their effect to size distribution or chemical composition. This discussion is based on their effect on size distribution.

Coarse mode particles are relatively insensitive to dilution conditions, the size and amount of these large particles don't change much. Sampling losses and re-entrainment of collected particles is more important factor. It is difficult to measure this mode reliably and the repeatability is a problem due to the nature of these particles. For the sake of repeatability pre-separation of these particles is advised. This can be done for example with impactor or cyclone.

Accumulation mode consists mainly from soot particles. Some volatile species can be on the surface of these particles depending on the conditions. There are two possibilities on how to measure this mode. One is to remove or differentiate the volatile species and the other is to try to mimic atmospheric conditions. Atmospheric conditions are difficult to mimic because they have high variations both spatially and temporally and therefore there is no universal conditions to select. Soot particle distributions from accumulation mode are very repeatable and could be very useful for comparison purposes between vehicles and technologies. Volatiles can be removed directly during the sampling by using thermodenuder or catalytic stripper. Afterwards they can be removed from the collected samples by using extraction, coulometry or thermal conditioning. Instead of removing volatiles the impact of volatiles can be reduced by using sampling conditions that prohibit or at least hinder the transfer of volatile species on the particle phase.

In roadside measurements a nucleation mode is detected. This implies to nucleation of some gaseous components (Harrison et al., 1999) (Weingartner et al., 1997). Particles in this mode consist mainly of hydrocarbons and sulphur although some metals from the fuel and engine oil additives can be found. Large fraction of volatile hydrocarbons and sulphur can be in this mode. The choice here is to decide how to measure these, should these compounds be measured from the gas phase or from the particles. There is no definite answer. The health effect studies don't yet have a definite answer on how toxic the nucleated nanoparticles are. Even if their effect on global environment or total mass emissions isn't significant, for immediate neighbourhood of the road their effect however could be substantial. Therefore the nucleation potential of the exhaust should somehow be measured or determined. One possibility would be to generate sampling conditions very favourable to nucleation and measure the amount of nucleating particles, although in this case the challenge of relating these measurements to the real world would be significant.

References

Abdul-Khalek, I.S., Kittelson, D.B., Graskow, B.R., Wei, Q., Brear, F., 1998. Diesel Exhaust Particle Size: Measurement Issued and Trends, SAE paper 980525.

Abdul-Khalek, I., Kittelson, D., Brear, F., 1999. The influence of dilution conditions on diesel exhaust particle size distribution measurements. SAE Paper 1999-01-1142.

ACEA, 1999, ACEA Programme on the Emissions of Fine Particles from Passenger Cars, Report, December 1999, Brussels, Belgium.

Ahlvik, P., Ntziachristos, L., Keskinen, J., Virtanen, A., 1998. Real Time Measurements of Diesel Particle Size Distribution with an Electrical Low Pressure Impactor, SAE Paper 980410.

Andersson, J.D., Wedekind, G.A., Hall, D., Stradling, R., Barnes, Ch., Wilson, G., 2000. DETR/SMMT/CONCAWE Particle Research Programme: Sampling and Measurement Experiences, SAE paper 2000-01-2850.

Bagley, S.T., Baumgard, K.J., Gratz, L.D., Johnson, J.H., Leddy, D.G., 1996. Characterization of Fuel and Aftertreatment Device Effects on Diesel Emissions, Health Effects Institute, Research Report No. 76, Cambridge, MA, USA.

Bell, S.P., Dickens, C.J., Feest, E.A., Smith, A.P., Tope, A.M., 1999. Experimental Assessment of Particulate Measurement Instrumentation, Report No. AEAT-4978, Oxfordshire, UK.

Biswas, P.; Measurement of high concentration and high temperature aerosols; In: Aerosol Measurement: Principles, Techniques and Applications, Eds. Willeke K. and Baron P.A., Van Nostrand Reinhold, New York, 1993.

Clark, N., 2000. Presentation to the CRC/CEC/JAMA Vehicle Exhaust Particulate Emissions Measurement Workshop, June 19, 2000, Paris, France.

EPA, 2000. Health Assessment Document for Diesel Exhaust, to become cited soon, Internet reference of final draft at http://www.epa.gov/ncea/dieslexh.htm.

Dickens, C. J., M. H. E. Ball, D. Booker, J. R. Donald, A. M. Tope and M. Hughes. 1997. Evaluation of Instruments for Vehicle Emission Particle Sizing. AEA Technology Report AEAT-1180, 69 pp.

Frisch, L.E., Johnson, J.H., Ledy, D.G., 1979. Effect of Fuels and Dilution Ratio on Diesel Particulate Emissions, SAE paper 790417.

Graskow, B.R., Kittelson, D.B., Abdul-Khalek, I.S., Ahmadi, M.R., Morris, J.E., 1998. Characterization of Exhaust Particulate Emissions from a Spark-Ignition Engine, SAE Paper 980528.

Graskow, B.R., Ahmadi, M.R., Morris, J.E., Kittelson, D.B., 2000. Influence of Fuel Additives and Dilution Conditions on the Formation and Emission of Exhaust Particulate Matter from a Direct Injection Spark Ignition Engine, SAE Paper 2000-01-2018.

Hall, D., Dickens, C.J., 2000. Measurement of the Numbers of Emitted Gasoline Particles: Genuine or Artefact?, SAE Paper 2000-01-2957.

Harrison R.M., Jones M., Collins G. ; Measurement of the physical properties of particles in the urban atmosphere ; Atmospheric environment 33 (1999) 309-321

Hinds, W.C. (1982) Aerosol Technology, John Wiley & Sons, New York, USA.

Hueglin Ch., Scherrer L., Burtscher H. ; An accurate, continuously adjustable dilution system (1:10 to 1:104) for submicron aerosols ; Journal of aerosol science, Vol 28, No 6, pp 1049-1055, 1997

Johnson, J. E. 1993. Hydrocarbon Oxidation in a Diesel Catalytic Converter. University of Minnesota M. S. Thesis, Minneapolis, MN.

Kasper, M., Matter, U., Burtcher, H., 2000. NanoMet: On-line characterization of nanoparticle size and composition. SAE 2000-01-1998.

Kayes, D., Hochgreb, S., 1998. Investigation of the Dilution Process for Measurement of Particulate Matter from Spark-Ignition Engines, SAE Paper 982601.

Kittelson, D. B., et al. 1990. Particulate Emissions from Diesel Engines: Influence of In-Cylinder Surface. SAE Paper No. 900645. Warrendale PA

Kittelson, D.B., Johnson, J.H., 1991. Variability in Particle Emission Measurements in the Heavy Duty Transient Test, SAE Paper 910738.

Kittelson, D.B., Sun, R., Blackshear, Jr P.L., Brehob, D.D., 1992. Oxidation of Soot Agglomerates in a Direct Injection Diesel Engine, SAE Paper 920111.

Kittelson, D.B., 1998, Engines and Nanoparticles: A Review, J. Aerosol Sci., Vol. 29, No. 5/6, pp. 575-588.

Kittelson, D., Arnold, M., Watts, W., 1999. Review of Diesel Particulate Matter Sampling Methods, Final report, January, 14, 1999, Minneapolis, USA. Internet Reference at http://www.me.umn.edu/centers/cdr/Proj_EPA.html.

Kittelson D. and Abdul-Khalek I., 1999. Formation of nanoparticles during exhaust dilution ; EFI members conference : ”Fuels, Lubricants, Engines & Emissions” ; University of Minnesota Department of Mechanical Engineering

Kittelson D. and Watts, W. 2000. Roadway measurements of diesel exhaust aerosols. 19th annual AAAR Conference, St. Louis, Missouri 2000.

Kittelson, D., Johnson, J., Watts, W., Bukowiecki, N., 2000. Diesel Aerosol Sampling in Atmosphere. SAE 2000-01-2122.

Koch W., Lödding H.,Mölter W. and Munzinger F. ; Verdünnungssystem für messung hochkonzentrierter aerosole mit optischen partikelzählern ; Staub – Reinhaltung der luft 48 (1988) 341-344

Kütz, S., Schmidt-Ott, A., 1992. Characterization of agglomerates by condensation-induced restructuring, J. Aerosol Sci., Vol.23, Suppl. 1, S357-S360.

Lüders H., Krüger M., Stommel P., Lüers B.; The role of sampling conditions in particle size measurements ; Sae Technical Paper Series 981374 ; 1998

MacDonald J.S., Plee, S.L., D´Arcy, J.B., Schreck, R.M., 1980. Experimental Measurements of the Independent Effects of Dilution Ratio and Filter Temperature on Diesel Exhaust Particulate Samples, SAE Paper 800185.

Maricq, M., Chase, R.E., Podsiadlik, D.H., Vogt, R., 1999. Vehicle Exhaust Particle Size Distributions: A Comparison of Tailpipe and Dilution Tunnel Measurements, SAE Paper 1999-01-1461.

Mayer, A., Czerwinski, J., Scheidegger, P., 1996. Trapping efficiency depending on particulate size. SAE Tech Pap. 960472.

McAughey, J., 2000. Vehicle Particulate Emissions, A Report Produced for European Commission – Directorate General III, May 2000, AEAT/R/ENV/0047 Issue 1, Oxfordshire, UK.

Ntziachristos, L., Samaras, Z., 2000a. Sampling conditions effects on real time particle measurements from a light duty vehicle. SAE 2000 Transactions Paper 2000-01-2049.

Ntziachristos, L., Samaras, Z., 2000b. Characterisation of exhaust particles from diesel and gasoline vehicles of different emission control technologies, 21st Century Emissions Technology International Conference, 4-5 December 2000, ImechE Headquarters, London, UK.

Plee. S.L., MacDonald. S.J., 1980. Some Mechanisms Affecting the Mass of Diesel Exhaust Particulate Collected Following a Dilution Process, SAE paper 800186.

Poon, W.S., Pui, D.Y.H., Liu, B.Y.H., 1993. A compact porous denuder for the sampling of atmospheric aerosol, J. Aerosol Sci., Vol. 24, Suppl. 1, S367-S368.

Reichel. S., Pishinger. F.F., Lepperhoff. G., 1983. Influence on Particles in Diluted Diesel Engine Exhaust Gas, SAE Paper 831333.

SAE Recommended Practice, 1989. Constant Volume Sampler for Exhaust Emissions Measurement – SAE J1094a in SAE Handbook, Volume 3: Engines, Fuels, Lubricants Emissions, and Noise, Sections 23-26, Warrendale, PA, USA.

Shi, J.P., Khan A.A., Harrison, R.M., 1999. Measurements of Ultrafine Particle Concentration and Size Distribution in the Urban Atmosphere, The Science of The Total Environment, Volume 235, Issues 1-3, 1 Pages 51-64.

Shi, J.P., Harrison, R.M., 1999. Investigation of Ultrafine Particle Formation during Diesel Exhaust Dilution. Environ. Sci. Technol., Vol. 33, pp. 3730-3736.

Turpin, B.J., Saxena, P., Andrews, E., 2000. Measuring and simulating particulate organics in the atmosphere: problems and prospects. Atm. Env. 34, 2983-3013.

Vartiainen M., McDow S.R., Kamens R.M. ; Water uptake by aerosol particles from automobile exhaust and wood smoke ; Chemosphere, vol 29, No 8,(1994) 1661-1669

Wedekind, B.G.A., et al. (2000). DETR/SMMT/CONCAWE Particle research programme: Heavy duty results. SAE 2000-01-2851, Warrendale PA.

Weingartner E., Keller W., Stahel W.A., Burtscher H., Baltensperger U. ; Aerosol emission in a road tunnel ; Atmospheric environment, vol 31, No 3 (1997) 451-462

Weingartner E., Baltensperger U., Burtcher H. ; Growth and structural change of combustion aerosols at high relative humidity ; Environmental Science Technology, vol 29, (1995), 2982-2986

Willeke, K., Baron, P.A., 1993, Aerosol Measurement: Principles, Techniques and Applications, Van Nostrand Reinhold, New York.

6. Measurement instrumentation

The purpose of this chapter is to briefly describe instruments available for particle measurements. A detailed review of particle measurement techniques can be found in a review report produced by Professor David Kittelson of the University of Minnesota for the US Environmental Protection Agency (Kittelson, 1999). Good reference book for particle measurement instruments is also Aerosol Measurement (Willeke and Baron, 1993).

6.1. Integrating concentration instruments

Since the purpose of the project is to measure size distributions, this section does not describe all of the available instruments for concentration measurements. It will only describe the ones that could be potentially used in the project.

6.1.1. Condensation particle counter (CPC)

Condensation particle counters measure total number concentration of particles. They can detect single particles and are especially used to detect ultrafine particles. In CPC particles are exposed to supersaturated vapor. This vapor condenses on the particles and the particles grow to the sizes that can then be detected with optical systems (Cheng in Willeke and Baron, 1993). Most commercial CPC's can measure concentrations up to 1000 particles/cm^3 in count mode, i.e. counting individual particles. Higher concentrations can be measured in photometric mode, where the concentration is determined by measuring the light extinction through the viewing volume. This mode is not as accurate as count mode and requires careful calibration. Different types and models of CPCs have different lowest detectable particle size. This has to be remembered when measuring and comparing measured concentrations with different types of CPCs.

6.1.2. Tapered element microbalance (TEOM®) mass monitor

In TEOM particle mass sample is collected on a filter mounted in a tapered oscillating element (Patashnick and Rupprecht 1980). The natural frequency of the tapered element depends on it's mass. Therefore the mass collected on a filter changes the frequency of a tapered element (Willeke & Baron, 1993). Electronic feedback system is used to detect frequency changes these changes are related to changes in mass of the tapered element. TEOM provides real-time mass concentration information. However volatile species have been identified as a problem for TEOM. Some gaseous species can condense on the filter or some of the species collected on the filter can evaporate giving inaccurate results.

6.1.3. Diffusion charger

In a diffusion charger a corona discharge from a high voltage wire generates air ions that charge aerosol particles. Combining the charger with aerosol electrometer results in electrical aerosol detector which is capable of measure particle concentrations.

The number sensitivity of diffusion charging is approximately proportional to Dp in molecular regime and to Dp^2 in continuum regime. To be able to detect different particle sizes some kind of classifier has to be used before charger. If particle classifier is not used diffusion charger response is related to an integral value of Dp which is sometimes called the Fuchs area.

In diffusion limited transfer of molecules onto particles (sticking coefficient =1), the total number of molecules transferring onto particles, in unit volume of gas, integrated over particle size gives the so-called Fuchs surface area (e.g. Gäggeler et al., 1989a) of the particles. It is a relevant quantity of particle concentration for diffusion mass transfer processes. In a diffusion charger, direct measurement of Fuchs surface is based on using unipolar ions as trace compounds transferring into particle phase. Previously, the technique has been applied to measure the same quantity to mimic radioactive decay product attachment to aerosol (Keskinen et al., 1991).

A diffusion charger is available as a part of the NanoMet system (Kasper, 1999).

6.2. Vehicle particulate emissions aerosol size instrumentation

This section briefly describes the most common instruments used for particle size distribution measurements

6.2.1. Electric Mobility Instruments

Electrical mobility aerosol analysers such as the SMPS are based on the movement of gas-borne particles carrying a known electric charge towards an electrode of opposite charge. These techniques are widely used in the laboratory, especially in particle formation studies, since they have the potential for very good size resolution in the range 0.004 to 1.0 μm diameter. However, their application in the field is largely restricted to the measurement of low concentrations of stable aerosols, such as may be found in environmental pollution monitoring. Electrical mobility analysers are fairly expensive to purchase, and require skill in the operation and interpretation of the data. However, for diesel particulate measurements they offer the capability of near-real time measurements over the applicable size range. The measurement of size distributions typically requires approximately 1-2 minutes and therefore this technique can, in principle, offer near real-time analyses.

Electric mobility instruments use a common electrical mobility analyser technique to fractionate size. An aerosol is passed through a charger, with the electrically charged particles then passing through a variable electric field in a mobility analyser. This acts like a filter to select out particles with a range of electrical mobilities, with particles smaller and larger than the chosen band precipitating in the instrument. An electrometer or a particle counter instrument then measures the particles that are allowed to pass through the analyser. The strength of the electric field that causes particles with a specific electric mobility to precipitate on the analyser surfaces can be varied to control the size of the particles that are allowed to pass through and be measured.

Electrical mobility analysers are widely used to size particles in the range 0.004 to 1μm volume equivalent diameter. Particles much smaller than this lower limit are difficult to charge, whereas multiple charging becomes a problem with micron-sized and larger particles. Electrical mobility analysers are the only high-resolution techniques for particles smaller than about 0.1 μm volume equivalent diameter.

Differential mobility analysers (DMAs) have been developed to capture the narrow range of particles that have a common trajectory within an electrical mobility analyser. They typically consist of an Electrostatic Classifier as the mobility analyser, which is coupled to a continuous flow condensation nucleus counter. The aerosol flow rate entering the instrument ranges from 0.1 to 1.0 $l\ min^{-1}$, although is normally operated at the flow rate of the CPC ($0.3\ l\ min^{-1}$). Particles larger than 1 μm aerodynamic diameter are initially removed in a single-stage impactor, since they may carry more electrostatic charge than the data reduction procedure permits, resulting in the propagation of large errors throughout the measured size distribution.

The aerosol is then passed through a bipolar charge equilibrator consisting of a ^{85}Kr radioactive source contained within the electrostatic classifier section. Emerging particles carry a Boltzmann distribution of charges (the overall charge is zero, but the aerosol contains well-defined proportions of particles carrying ±1, ±2, ±3 charges etc. The electrode voltage is initially set to a low positive potential; particles that have a narrow range of high electrical mobilities (smallest particles) enter the gap and are collected by the detector as a 'monodisperse' aerosol. As the electrode voltage is increased, the sizes of particles exiting the electrostatic classifier also increase, since the electrical mobility of the particles that enter the gap at the base of the electrode decreases. As the particle size increases above 0.05 μm volume equivalent diameter, the aerosol begins to consist of several monodisperse sub-fractions corresponding to the different negative charge levels allowed by the Boltzmann charge equilibrium. Thus, the signal recorded by the detector during the measurement sequence corresponds to the actual number-size distribution, modified by the presence of a known proportion of multiply-charged particles. The analyser software corrects for these multiply-charged particles up to 6 charges per particle.

6.2.1.1. Scanning Mobility Particle Sizer (SMPS)

Scans can be achieved in as little as 60 s at very high resolution (64 channels per decade of size). In the Scanning Mobility Particle Sizer (SMPS) the electric field strength in the electrical classifier section is varied monotonically, at the same time making particle number concentration measurements in rapid succession (as much as 10 times per second) using a condensation nuclei counter. The measurement cycle consists of repeated ramps of the central electrode voltage on an exponential scale, increasing from a defined minimum value to maximum field strength, then decreasing the field strength back to the minimum value. The particles entering the sample extraction slot of the classifier will have a monotonic variation in electrical mobility if the electric field strength is varied monotonically. Hence, after making allowances for the finite transit times of the particles within the classifier and from the extraction slot to the condensation nucleus counter, the entire size distribution of the incoming aerosol can be scanned both accurately and rapidly. As the voltage is scanned rather than stepped, the number of size intervals is primarily limited by particle residence time and the speed at which the particles can be counted by the CNC with scans of 128 particle-size intervals in as little as 30 s.

Particle concentration or size changes during the scan may bias the measured size distribution, giving problems over use in transient speed and engine load test cycles. The SMPS can also be run in a single size mode as well as in a scanning mode. In the single size mode it measures a single particle mobility size range continuously with a time resolution of a few seconds. In this mode it can be used for transient particle size measurements, one size range at a time (Greenwood, et. al. 1996). However, a minimum of 3 to 5 size ranges are required to approximately describe the submicrometer size distribution, such that 3 to 5 transient tests or instruments are required to obtain one size distribution, which makes the approach time consuming and/or expensive.

Both the SMPS and EAA (below) require a pre-classifier to remove super-micron particles. The SMPS can operate at lower dilution ratios than EAA, such as the 10 - 30:1 ratios typically found in dilution tunnels. However, under these conditions the instrument fouling becomes a concern. The SMPS operates most effectively at dilution ratios of around 100:1 for typical diesel exhaust aerosols. Here is an example of how instruments used to obtain the aerosol size distribution affect the conditions under which the aerosol is collected. The size distributions obtained under 30:1 dilution may be quite different from those obtained from 1,000:1.

6.2.1.2. Differential Mobility Particle Sizer (DMPS)

The DMPS (Pui and Swift 1995) also sizes particles by electrical mobility using an electrical mobility analyser. Sampled particles are exposed to a bipolar charger (rather than the unipolar charger of the EAA). The charged particles enter a mobility analyser section of the DMPS and rather than acting as an integrating low-pass filter, only particles with a specific range of electric mobility are allowed to pass through the differential mobility analyser and be measured. In contrast to the continuous scans of the SMPS, discrete steps vary the applied voltage within the mobility analyser. A pre-classification stage, such as an impactor or cyclone, must be used when sampling diesel exhaust in order to prevent the introduction of measurement errors from particles larger than 1.0 µm (Yeh, 1993).

6.2.1.3. Electrical Aerosol Analyser (EAA)

The EAA is the instrument that has been most commonly used in early studies in the U.S. (Liu et al 1974., Liu and Pui 1975, Dolan et al.1980, Groblicki and Begeman 1979, Fang and Kittelson 1984, Baumgard and Kittelson 1985, Baumgard and Johnson 1992, Bagley et al., 1996) for diesel aerosol size distribution measurements, although some use in Europe has been reported. Within the EAA, sampled particles are exposed to unipolar positive ions and become electrically charged. The charged particles again enter a mobility analyser section of the EAA, acting as a low-pass filter, precipitating particles having high electrical mobility. Measurement of the current carried by the charged particles is conducted using an electrometer mounted downstream of the mobility analyser section. Stepping the mobility analyser through 11 voltages (7 used typically) and measuring the current carried by the particles with an electrometer generates a particle-size distribution. As for the SMPS and DMPS a pre-classification stage, such as an impactor or cyclone, must be used when sampling diesel exhaust in order to prevent the introduction of measurement errors from particles larger than 1.0 µm (Yeh, 1993). The effective particle-size range of the EAA is 10 nm to 0.5 µm, with a sample cycle of approximately 2 to 3 minutes. Thus the EAA is sensitive to errors if particle number concentrations change within the time interval of a single scan of EAA voltages.

This has typically precluded the use of the EAA over transient speed and engine load test cycles. Hammerle, et al. (1994) and Dolan, et al. (1980) used bag samples to collect particles over transient test cycles for later size analysis by the EAA but diffusional particle losses of up to 50% after 20 minutes were reported by Hammerle et al (1994).

Diesel aerosol measurements with the EAA typically require the use of relatively high dilution of diesel exhaust samples (300:1 to 1000:1) to prevent electrometer saturation. Similar ranges of dilution (to 1000:1) have been reported for roadway measurements, but typical laboratory dilution tunnels operate with dilution ratios ranging from approximately 10:1 to 20:1. Thus, additional dilution of the exhaust sample is needed prior to entering the EAA (Baumgard and Kittelson 1985), (Baumgard and Johnson 1992), (Bagley, et. al. 1996).

6.2.1.4. Nanometer Differential Mobility Analyser (nano-DMA)

A new, nanometer differential mobility analyser (nano-DMA) (Chen and Pui 1997, Chen, et. al. 1996, 1998, Hummes, et. al. 1996) has been described. It is optimised for nanometer size particles, using a flow geometry to minimise residence time and diffusional losses. Scans of particle size between 3 - 50 nm can be completed at high resolution in approximately 10 seconds. This particle size range roughly corresponds to the complete nucleation mode size range. The nano-DMA has not been used widely, and there is no established database of results. However, this appears to offer significant scope for understanding the nature of gas to particle conversion in formation of nuclei-mode particles.

6.2.2. Inertial Mobility Instruments

6.2.2.1. Cascade impactors

An impactor stage consists of a series of jets beneath which is situated a flat collection medium at a pre-set distance. Aerosol passing through each jet is directed against the collection medium causing the fluid streamlines to be deflected through 90°. Particles with high inertia are unable to follow the streamlines and impact on the collection medium while particles with a sufficiently low inertia follow the streamlines and miss the collection plate.

Impactors measure the inertia-based aerodynamic diameter (d_{ae}) of aerosol particles, defined as the diameter of a sphere with a density of 1 g cm^{-3} that has the same settling velocity as the particle under consideration:

The cascade impactor consists of several impactor stages in series each with greater collection efficiency with respect to aerodynamic diameter. Cascade impactors are used to measure mass size distributions. Collection substrate of each stage is weighted before and after the measurement. From the difference in weight, collected mass in each stage and the mass based size distribution can be determined. This substrate changing and weighing takes time and limits the number of samples that can be taken. Measured mass distributions are integral over the sampling time so they cannot provide real-time information.

There is lot of varying impactor designs for different applications. Good reference can be found in a book by Willeke and Baron (1993). Following descriptions cover only the most common impactors.

6.2.2.1.1. Andersen MkIII Impactor

The Andersen MKIII cascade impactor is a conventional 8-stage cascade impactor operating at 28.3 L/min, with a range of 0.4 – 10 μm. It is also limited in its minimum size point. However, it does offer some advantages as it is a well-established technique of known accuracy and precision, and has been used routinely for the collection of samples for subsequent chemical analysis.

6.2.2.1.2. Micro-Orifice Uniform Deposit Impactor (MOUDI):

The MOUDI (Marple, et al 1991) is a 10 stage impactor with the four lower stages having micro-orifice impaction plates. The cut points at the nominal flow rate of 30 L/min range from 0.056 - 10 μm in aerodynamic diameter with a total pressure drop across the impactor of 0.3 atmospheres. The combustion aerosol nucleation mode is composed primarily of volatile organic material, thus care is required to avoid evaporative losses of volatile organics, particularly the condensed organic material. The MOUDI does however cover the full size range for the mass size distribution of diesel exhaust because it. However, the MOUDI provides no size breakdown of aerosols < 50 nm nor does it provide data on the number distribution. Data are obtained after gravimetric analysis of the MOUDI impaction substrates so the MOUDI does not provide results in real-time. The diesel aerosol is normally diluted 10:1 or more before sampling to avoid overloading the impactor substrates from higher particulate concentrations. However, undiluted exhaust can be sampled directly if the sampling times are very short and care is taken not to overload the impaction substrates. The MOUDI has been used extensively to determine the size distribution of diesel aerosols in underground mines (Cantrell and Rubow 1993).

6.2.2.1.3. Nano-Micro-Orifice Uniform Deposit Impactor (Nano-MOUDI)

The nano-MOUDI (Marple, et al 1994) has 13 cut-sizes ranging from 0.010 to 18 µm and is designed to obtain four cut-sizes per decade. For cut-sizes above 50 nm, micro-orifice technology alone is sufficient to obtain the selected cut-points, but for cut-sizes below 50 nm micro-orifice nozzle technology is combined with low pressure operation. Again, there is potential for evaporative losses. Gravimetric analysis is used to determine the mass collected on aluminium foil substrates and a final stage filter. These substrates may be analysed to determine the chemical composition of the mass collected on each stage

6.2.2.2. Electrical Low-Pressure Impactor (ELPI)

The Electrical Low Pressure Impactor (ELPI, Dekati Ltd) is designed to measure size distribution of aerosol particles in the size range from 0.03 to 10 µm aerodynamic diameter (Dekati, 1996, Marjamäki et al. 2000). The instrument combines electrical detection with conventional cascade impactor (Keskinen et al., 1992). The instrument is a multistage, multi-jet device that fractionates particles into size classes based on their inertia. The ELPI is a 13-stage cascade device that is normally operated at approximately 10 l min^{-1}.

As aerosol first enters the ELPI it passes through a unipolar positive polarity charger which uses a corona discharge wire to produce an electrostatic charge on the particles. The particles are then size classified in the cascade impactor, which is operated at reduced pressure. The reduction in pressure changes the properties of the gas associated with the inertia of the particles and this allows even smaller particles to be classified than might otherwise be expected in an inertial-based device. When a particle has been classified it impacts on one of the stage collection plates which are electrically isolated from the other stages. Each plate is connected to a current amplifier and the discharge from the electrostatically charged particle is measured. The current measured from each stage is proportional to the number of particles collected and a number-based aerodynamic particle size distribution can be determined from certain properties of the particle, charger and impactor stages.

Using the current amplifiers and charging of the particles to determine the particle size distribution of an aerosol is a number-based technique whereby the number of particles collected is measured directly (by current discharge) and the mass-based distribution is calculated from the number-based data. This mode of operation of the ELPI is known as the number mode. The ELPI can also be used as a conventional impactor by determining the mass of material on each stage directly using either gravimetric or chemical techniques (mass mode).

However, some uncertainties regarding calibration have been reported in the upper end of the ELPI size range. In general however, agreement between the ELPI and SMPS has been observed over their common operating ranges (Dickens, et. al. 1997, Moon and Donald 1997, Maricq, 1999, Maricq, 2000, Marjamäki et al., 2000). This reinforces the importance of established calibration procedures when using different instruments especially where the principle of measurement differs.

It is noted that, in the basic configuration, the lower size limit of ELPI is 30 nm and it will not detect the bulk of nanometer particles produced by new technology engines. However currently additional filter stage is available for ELPI. This will increase the size range to cover below 30 nm particles. This filter stage has not been used widely, and there is no established database of results

The lower size limit is further compromised by the fact that the last few stages operate at rather low pressures, which may result in evaporation of semi-volatile particles. Despite these limitations the ELPI is used for diesel particulate measurements because it is a versatile instrument, capable of spanning a wide range of particle size and concentration, in real-time, producing both number and volume size distributions. In particular, the ELPI is quite useful because it provides information over a wide size range, 30 nm to 10 µm under transient test conditions.

6.2.2.3. Quartz Crystal Microbalance

Low-pressure impactors operate by passing the flow through a critical orifice, usually located towards the bottom of the stack of collection stages. The upper part of the analyser therefore operates as a conventional impactor, whereas efficient sub-micron separation can also take place in the low pressure section because the slip correction factor is greatly increased, reducing the aerodynamic drag on the particles. The QCM is one such instrument, which uses vibrating quartz crystal sensors to measure mass-size distributions in the range from 0.05 to 25 µm aerodynamic diameter. It has been noted however that this type of instrument is susceptible to diffusion-based losses of particles <0.5 µm, and shows unpredictable behaviour with electrostatically charged aerosols. The quartz crystal impactor grossly underestimates the concentrations of diesel particles throughout its operating range (Moon and Donald, 1997). Apparently diesel particles do not couple well with the vibrating surfaces of the quartz substrates. This causes the instrument to underestimate deposited mass.

6.2.3. Radioactive Tracer Instruments

The attachment of a radioactive tracer to particles allows the measurement of particle radioactivity to be related to particle surface area.

Epiphaniometer:

The epiphaniometer (Gaggeler, *et al* 1989a, Gaggeler, *et al* 1989b) is an instrument that measures the surface concentration of aerosol particles in both the nuclei and accumulation mode size ranges. The epiphaniometer is most sensitive to particles in the accumulation mode, but Gaggeler, *et al* 1989a reported successfully measuring silver particles between 20 and 90 nm that were agglomerates formed from smaller primary silver particles. In an epiphaniometer, aerosol is passed through a charging chamber where lead atoms created from a decaying actinide source transport by Brownian motion and attach to the particle surfaces. The particles are transported through a capillary to a collecting filter. The epiphaniometer uses a surface barrier detector to measure the level of radioactivity of the collected particles. This radioactivity is proportional to the particle’s Fuchs surface area and follows Fuchs theory of attachment of radioactive isotopes. Because of the short half-life of the lead isotopes, the filter does not become saturated and essentially real-time radioactivity measurements can be made. A pre-classifier, such as a DMA, may be used before the epiphaniometer to allow a pre-determined size range of particles to enter the instrument.

6.2.4. Other Sizing Instruments

6.2.4.1. Aerodynamic particle sizer (APS)

The aerodynamic particle sizer (APS; TSI, US) has been used by a few laboratories for exhaust particle measurements. This instrument sizes particles by aerodynamic diameter in the size range from about 0.5 to 10 µm diameter. However, the majority of the mass and number of particles lie below the lower detection limit of the instrument and may display an artefact (Baron, Mazumder and Cheng, 1993).

6.2.4.2. Diffusion Batteries

Diffusion batteries were developed to determine particle diffusion coefficients (Cheng 1993), and have been used for size characterisation of 1 nm to 100 nm aerosols for more than 50 years by deriving particle size from diffusion characteristics. Diffusion batteries separate particles by their diffusion mobility. Diffusion batteries are typically used with a switching valve to vary the effective diffusional path length, and a CPC counter for measuring particle number concentrations to obtain a particle size distribution between approximately 0.5 nm and 50 nm. Switching diffusion batteries have been used to determine particle size versus number concentration for diesel PM (Dolan et al. 1980, Baumgard and Kittelson). They have typically shown good agreement with electrical mobility and inertial impaction sizing methods where measurement ranges overlap.

A parallel flow diffusion battery, PFDB (Cheng and Yeh 1984, Degobert 1988), has been used to measure particle-size in diesel exhaust in the 3 nm to 0.5 μm size range over the light-duty, FTP test cycle using a standard, single dilution, EPA-style CVS dilution tunnel at dilution ratios of approximately 8:1 to 10:1 (Cheng and Yeh 1984). The PFDB was used with a low-pressure cascade impactor to allow classification of larger particles and to provide a necessary 0.7 μm pre-classification cut-point (Cheng and Yeh 1984). A similar device was developed (Boulad and Diouri, 1988) and used for DPM size characterisation (Degobert 1988) with an 8-stage cascade impactor from 0.35 μm to 7.5 μm, and diffusion battery with 5 parallel bead-beds covering 8 nm to 0.35 μm. Advantages of this type of diffusion battery measurement procedure include; direct filter mass measurement procedures, ability to integrate particle mass measurements for each size range to be over transient engine operating conditions, and similarity to actual diffusion-deposition mechanism for fine particles in lung tissue. Disadvantages include; potential difficulty in resolving the (typically) very small mass concentration of ultra-fine nuclei-mode particles, and errors associated with the data inversion techniques. It might be possible to combine the parallel diffusion battery approach with particle detection using CNCs. This would give near real time response, but would require multiple CNCs.

6.2.4.3. NanoMet

NanoMet (Kasper et al., 2000) is a combination instrument including rotating disk diluter, size classification system, and detection instruments (such as diffusion charger, PAS). According to Kasper and co-workers it uses centrifuge and diffusion battery for size classification. However the size classification part is still under development (Kasper et al., 2000).

6.3. Chemical Composition Instrumentation

This section describes briefly on-line chemical composition instruments. The possible chemical analysis methods for this project have been described in appendix 1.

6.3.1. Photoemission Aerosol Instruments

It has been recognised that the chemical composition of a diesel particle might influence its health impact when deposited in the human lung. Unburned hydrocarbons, such as polycyclic aromatic hydrocarbons (PAH’s), from incomplete combustion are recognised as potent mutagens and carcinogens. Historically, analysis of the PAH content of diesel particle matter has been by particle collection on filters, extraction of the soluble organic fraction and PAH identification by chromatography and mass spectrometry. Aerosol photoemission sensors have been developed for in-situ measurement of total particle bound PAH's and provide a potential alternative method for PAH quantification (Burtscher and Siegmann 1993). However this method does not quantify individual PAH compounds. PAH is a very complex mixture of individual compounds and the relative contribution of individual PAH is dependant on several factors such as fuel, driving conditions, engine type etc. To get information about the individual PAH compounds chemical analysis has to performed (see Appendix 1).

6.3.1.1. Photoelectric Aerosol Sensor (PAS)

Photoelectric aerosol sensors (Burtscher and Siegmann 1993, Burtscher, et al 1993, Hart, et al 1993) have been used to quantify the total PAH content associated with diesel particulate matter and other combustion-mode aerosols. Now PAS is also available as a part of NanoMet system (see above). Typically, the sample passes through an electrical condenser to remove any electrical charge. Following irradiation with a UV laser or flash lamp in a photoemission chamber where particles with photoelectric work functions below the photon energy of the UV source emit electrons and become positive ions (Weiss 1997). The photoemission chamber has a small electric field that precipitates out the high mobility electrons and negative ions. The positive particles are collected on a filter and the resulting current measured by an electrometer. The intensity of the particle photoemission is linearly related to the amount of particle-bound PAH's and hence particle surface area, with a detection limit of about 1 ng/m^3 with a time resolution of about 1s (Burtscher and Siegmann 1993). This method does not quantify individual PAH compounds.

6.3.2. Mass Spectroscopy Instruments

Chemical composition by time-of-flight mass spectrometry is well established and can be used to identify specific chemical components in individual aerosol particles. However, techniques are not yet sufficiently size-sensitive at the lower end of the accumulation mode or the nucleation mode of diesel exhaust aerosols.

6.3.2.1. Aerosol Time-of-Flight Mass Spectrometer (ATOFMS)

The ATOFMS (Noble and Prather 1996 and 1998, Gard, et al 1997, Silva and Prather 1997) is unique in that it provides both real-time measurement of aerodynamic size and chemical composition of individual particles from a polydisperse aerosol. The instrument can analyse up to 600 particles per minute and can measure particles down to 0.3 μm in diameter. The spectrometer includes two oppositely charged reflectrons that measure both positive and negative ions and provides good characterisation of inorganics and light and heavy organics. Silva and Prather (1997) found the chemical composition of exhaust particles to be related to the size of the particle being measured and attribute this to the formation mechanism of the particle. Larger automobile exhaust particles were found to be inorganic while smaller particles were found to be mainly organic. However, nuclei mode particles were not characterised. The authors also reported finding platinum, cerium, and molybdenum in exhaust particles.

6.3.2.2. On-Line Aerosol Mass Spectrometer

This instrument (Weiss, 1997) is similar in design to the ATOFMS and also provides both real-time particle sizing and composition information. The lower limit for aerodynamic sizing is around 0.3 to 0.4 μm because particles smaller than this do not scatter sufficient light to be measured for aerodynamic sizing. Particles larger than the upper limit on particle size of about 50 μm quickly clog the extremely small nozzles and orifices in the instrument. The on-line mass spectrometer can analyse up to 120-600 particles per minute. The on-line mass spectrometer uses a single ion detector that characterises inorganic and lighter organic material well but does not provide adequate resolution for more complex organics. It has been used to measure the concentration of cerium in diesel particulate matter that had been added to the fuel of a DI diesel engine. Metal-based fuel additives such as cerium are added to diesel fuel so as to act as an oxidation catalyst to assist in the regeneration of diesel exhaust filters. Determination of the fate of these metals in diesel exhaust adds to the understanding of their impact on diesel emissions.

6.3.2.3. Particle-Beam Mass Spectrometer (PBMS)

This method uses a mass spectrometer to determine the composition of the volatile organic and inorganic components of particles that have been collected on an electrometer (Ziemann, 1995). An aerosol travels through a differential mobility analyser that allows only particles of a selected size to pass through. A particle beam is then generated by sending the charged particles selected by the DMA through a sequence of openings that concentrate the particles into a narrowing beam. The particle beam is then directed at an electrometer that acts as a particle collector. When sufficient particle mass is collected, the electrometer is heated to about 200^o C, driving off the volatile organics and inorganics which are analysed by a mass spectrometer. This method allows the chemical characterisation of the diesel particulate matter volatile material within a specific size. The collection of the particles allows sufficient mass for the mass spectrometry to be performed on nano-particles. There are currently no published results from this work.

References:

Bagley, S. T., K. J. Baumgard, L. D. Gratz, J. H. Johnson, and D. G. Leddy. 1996. Characterization of Fuel and Aftertreatment Device Effects on Diesel Emissions. Health Effects Institute Research Report Number 76, 88 pp.

Baron, P. A., M. K. Mazumder and Y. S. Cheng. 1993. Chapter 17 Direct Reading Techniques Using Optical Particle Detection. In Aerosol Measurement Principles Techniques and Applications, K. Willeke and P. Baron editors, Van Nostrand Reinhold, NY, NY., p. 381-409.

Baumgard, K.J. and J. H. Johnson. 1992. The Effect of Low Sulfur Fuel and a Ceramic Particle Filter on Diesel Exhaust Particle Size Distributions. Technical Paper Series, No. 920566, SAE: Warrendale, PA.

Baumgard, K.J. and D. B. Kittelson. 1985. The Influence of a Ceramic Particle Trap on the Size Distribution of Diesel Particles. Technical Paper Series, No. 850009, SAE: Warrendale, PA.

Boulaud, D. and M. Diouri. 1988. A New Inertial and Diffusional Device (SDI 2000). J. Aerosol Sci., Vol. 19(7), pp. 927-930.

Burtscher, H., D. Matter, and D. Steiner. 1993. Characterization of Soot Particles by In-Situ Measurement with Different Aerosol Analysis Tools. J. Aerosol Sci. , Vol. 23, pp. 65-67.

Burtscher, H. and H. C. Siegmann. 1993. Photoemission for In Situ Analysis of Particulate Combustion Emissions. Water, Air, and Soil Pol., Vol. 68: 125-136.

Cantrell, B. K. and K. L. Rubow. 1993. Measurement of Diesel Exhaust Aerosol in Underground Coal Mines. Bureau of Mines IC 9324, p. 11-17.

Chen, D. R. and D.Y.H Pui. 1997. A Novel Unipolar Aerosol Charger. Annual meeting of the AAAR, Denver, CO, October 13-17.

Chen, D. R., D.Y.H. Pui, D. Hummes, H. Fissan, F. R. Quant and G. J. Sem. 1996. Nanometer Differential Mobility Analyser (Nano-DMA): Design and Numerical Modelling. J. Aerosol Sci. Vol. 27 Supplement 1 pp. S137-S138.

Chen, D. R., D.Y.H. Pui, D. Hummes, H. Fissan, F. R. Quant and G. J. Sem. 1998. Design and Evaluation of a Nanometer Aerosol Differential Mobility Analyzer (Nano-DMA). J. Aerosol Sci. Vol. 29, No. 5/6, pp. 497-509.

Cheng, Y.S. 1993. Condensation Detection and Diffusion Size Separation Techniques. In Aerosol Measurement, K. Willeke and P.A. Baron, eds. Van Nostrand Rheinhold: New York, NY, pp. 427-451.

Cheng, Y.S. and C. H. Yeh. 1984. Analysis of Screen Diffusion Battery Data. Am. Ind. Hyg. Assoc. J., 45(8):556-561.

Degobert, P. Emissions Diesel, Aspects Physico-Chimiques. 1988. 5 ème Symp. Sur la Recherche en Matière de Pollution Atmosphériqe, Strasbourg, March 22-25, 13 p, (in French).

Dekati Ltd (1996) Electrical Low Pressure Impactor (ELPI) - User Manual,

Dickens, C. J., M. H. E. Ball, D. Booker, J. R. Donald, A. M. Tope and M. Hughes. 1997. Evaluation of Instruments for Vehicle Emission Particle Sizing. AEA Technology Report AEAT-1180, 69 pp.

Dolan, D.F.and D.B. Kittelson 1979. Roadway measurements of diesel exhaust aerosols. SAE Technical Paper Series No. SAE 790492. Warrendale PA

Dolan, D.F., D.B. Kittelson, and D.Y.H. Pui. 1980. Diesel Exhaust Particle Size Distribution Measurement Techniques. SAE Technical Paper Series, No. 800187.

Fang, C.P., and D. B. Kittelson. 1984. The Influence of a Fibrous Diesel Particulate Trap on the Size Distribution of Emitted Particles. SAE Technical Paper Series, No. 840362.

Gaggeler, H.W., U. Baltensperger, M. Emmenegger, D. T. Jost, A. Schmidt-Ott, P. Haller, and M. Hofmann. 1989a. The Epiphaniometer, A New Device for Continuous Aerosol Monitoring. J. Aerosol Sci., Vol. 20, No. 5, pp. 557-564.

Gaggeler, H.W., U. Baltensperger, D.T. Jost, M. Emmenegger, and W. Nageli. 1989b. Applications of the Epiphaniometer to Environmental Aerosol Studies. J. Aerosol Sci., Vol. 20, No. 8, pp. 1225-1228.

Gard, E., J.E. Mayer, B. D. Morrical, T. Dienes, D. P. Ferenson, and K. A. Prather. 1997. Real-time Analysis of Individual Atmospheric Aerosol Particles: Design and Performance of a Portable ATOFMS. Anal. Chem., Vol. 69, No. 20, pp. 4083-4091.

Greenwood, S.J., J. E. Coxon, T. Biddulph and J. Bennett. 1996. An Investigation to Determine the Exhaust Particulate Size Distributions for Diesel, Petrol, and Compressed Natural Gas Fuelled Vehicles. SAE Technical Paper Series, No. 961085.

Groblicki, P.J. and C. R. Begeman. 1979. Particle Size Variation in Diesel Car Exhaust. SAE Technical Paper Series, No. 790421.

Hammerle, R. H., D. A. Ketcher, R. W. Horrocks, G. Lepperhoff, G. Hüthwohl, and B. Lüers. 1994. Emissions from Current Diesel Vehicles. SAE Technical Paper Series, No. 942043.

Hart, K.M., St. R. McDow, W. Giger, D. Steiner, and H. Burtscher. 1993. The Correlation Between In-Situ, Real-Time Aerosol Photoemission Intensity and Particulate Polycyclic Aromatic Hydrocarbon Concentration in Combustion Aerosols. Water, Air, and Soil Pollution, Vol. 68, pp. 75-90.

Hinds, W.C. (1982) Aerosol Technology, John Wiley & Sons, New York, USA.

Horton, K.D., Ball, M.H.E. and Mitchell, J.P. (1992) The Calibration of a California Measurements PC-2 Quartz Cascade Impactor (QCM). J. Aerosol Sci. 23(5), 505-524.

Hummes, D., S. Neumann, H. Fissan, D. R. Chen, D. Y. H. Pui, F. R. Quant and G. J. Sem. 1996. Nanometer Differential Mobility Analyzer (Nano-DMA): Experimental Evaluation and Performance Verification. J. Aerosol Sci. Vol. 27 Supplement 1 pp. S136-S137.

Kasper, M. 1999. NanoMet: On-line characterization of nanoparticle size and composition. 3rd International ETH-Workshop on nanoparticle measurement.

Kasper, M., Matter, U., Burtcher, H., 2000. NanoMet: On-line characterization of nanoparticle size and composition. SAE 2000-01-1998.

Keskinen, J., Lehtimäki, M., and Graeffe, G. (1991) Radon decay product attachment rates in dwellings. J. Aerosol Sci. 22, 765-771.

Keskinen, J., Pietarinen, K., Lehtimäki, M. (1992) Electrical Low Pressure Impactor. J. Aerosol Sci. 23, 353-360.

Kittelson, D. B. 1999. Review of Diesel Particulate Matter Sampling Methods. USEPA. Downloadable from WWW at Centre for Diesel Research, University of Minnesota. http://www.me.umn.edu/centers/cdr/Proj_EPA.html.

Liu, B.Y.H and Agarwal JK 1974. Experimental observation of aerosol deposition in turbulent flow. J. Aerosol Sci. 5, 145-155.

Liu, B.Y.H and D. Y. H. Pui. 1975. On the Performance of the Electrical Aerosol Analyzer. J. Aerosol Sci., 6:249-264.

Liu, B.Y.H. and D. Y. H. Pui. 1974. A Submicron Aerosol Standard and the Primary, Absolute Calibration of the Condensation Nucleus Counter. J. of Colloid Interface Sci., 47:155.

Maricq, M. 1999. Vehicle Particulate Emissions: A Comparison of ELPI, SMPS and Mass Measurement. Proceedings of the 3. Nanomet Meeting, Zurich.

Maricq M., Chase, R.E., Podsiadlik, D.H. and Vogt, R. 1999. Vehicle Exhaust Particle Size Distributions: A Comparison of Tailpipe and Dilution Tunnel Measurements SAE technical Paper series 1999-01-1461. Warrendale, PA

Maricq, M., Podsiadlik, D.H., Chase, R.E., 2000. Size distributions of motor vehicle exhaust PM: A comparison between ELPI and SMPS measurements. Aerosol Sci. Techn. 33:239-260.

Marjamäki, M., Keskinen, J., Chen, D. and Pui, D.Y.H. (2000) ‘Performance evaluation of the electrical low pressure impactor (ELPI)’, J. Aerosol Science 31 249-261.

Marple, V. A, K. L. Rubow and S. M. Behm. 1991. A Microorifice Uniform Deposit Impactor (MOUDI): Description, Calibration, and Use. J. Aerosol Sci. Technol., 14:434- 446.

Marple, V. A., K. L. Rubow, and B. A. Olson. 1994. Low Pressure Stages for the Micro-orifice Uniform Deposit Impactor (MOUDI). Fourth International Aerosol Conference Abstracts, ed. R.C. Flagan, Vol. 2, 6 pp.

Mitchell, J.P., Costa, P.A. and Waters, S. (1988) An Assessment of an Andersen Mark-II Cascade Impactor. J. Aerosol Sci. 19(2), 213-221.

Moon, D. P. and J. R. Donald. 1997. UK Research Program on the Characterisation of Vehicle Particulate Emissions. (Contract Report for the Department of the Environment, Transport and the Regions and the Society of Motor Manufacturers and Traders). ETSU-R98, 90 pp.

Noble, C. A. and K. A. Prather. 1996. Real-time Measurement of Correlated Size and Composition Profiles of Individual Atmospheric Aerosol Particles. Environ. Sci. Technol., Vol. 30, pp. 2667-2680.

Patashnick, H. and Rupprecht. 1980. A new real time aerosol mass monitoring instrument: The TEOM. In Procedings: Advances in Particulate Sampling and Measurement, ed. W.B. Smith, p. 264, EPA-600/9-80-004. U.S. Environmental Protection Agency.

Pui, D.Y.H. and D.L. Swift. 1995. Direct-Reading Instruments for Airborne Particles. Ch. 16 in Air Sampling Instruments for Evaluation of Atmospheric Contaminants. Ed. By B. S. Cohen, and S. V. Hering. ACGIH, Cincinnati, OH, 8 th Edition, pp. 337 – 368.

Silva, P.J. and K.A. Prather. 1997. On-line Characterization of Individual Particles from Automobile Emissions. Environ. Sci. Tech., Vol. 31, pp. 3074-3080.

Weiss, M. 1997. An On-line Mass Spectrometer for Aerosols: Development, Characterization and Applications. Ph. D. Dissertation, Delft University of Technology, Netherlands.

Willeke, K., Baron, P.A., 1993, Aerosol Measurement: Principles, Techniques and Applications, Van Nostrand Reinhold, New York.

Yamano N. and Brockmann JE. 1989. Aerosol sampling and transport efficiency calculation (ASTEC) and application to Surtsey/DCH aerosol sampling system. US Nuclear Regulatory Commission, Report NUREG/CR-5252.

Yeh, H. 1993. Chapter 18 Electrical Techniques. In Aerosol Measurement Principles Techniques and Applications, K. Willeke and P. Baron editors, Van Nostrand Reinhold, NY, NY., p. 410-426.

Ziemann, P., et al. 1995. Measurement of Particle Induced Nucleation and Growth in Low Pressure Chemical Vapor Deposition Systems with the Particle Beam Mass Spectrometer. J. Aerosol Sci. Vol. 26, Suppl. 1, p. S633-S634

7. Recommendations and conclusions

7.1. Sampling and diluting

The chosen sampling and diluting concept affects the measurement result by two different mechanisms: a) losses of particles, b) possibility of gas to particle conversion.

Particle losses are most important for coarse mode measurement. For the sake of repeatability pre-separation of these particles is advised. This can be done for example with impactor or cyclone.

In the tailpipe conditions, the particles are normally solid, accumulation mode particles. Soot particle distributions from accumulation mode are very repeatable and could be very useful for comparison purposes between vehicles and technologies. Volatiles can be removed directly during the sampling by using thermodenuder or catalytic stripper. Afterwards they can be removed from the collected samples by using extraction, coulometry or thermal conditioning. Instead of removing volatiles the impact of volatiles can be reduced by using sampling conditions that prohibit or at least hinder the transfer of volatile species on the particle phase.

In roadside measurements a nucleation mode is detected. The health effect studies don't yet have a definite answer on how toxic the nucleated nanoparticles are, but for immediate neighbourhood of the road their effect could be substantial. Therefore the nucleation potential of the exhaust should somehow be measured or determined. One possibility would be to generate sampling conditions very favourable to nucleation and measure the amount of nucleating particles, although in this case the challenge of relating these measurements to the real world would be significant.

Recommendation:

- Solid particles should be measured. There is yet insufficient comparison data to decide the exact dilution system. However denuder would offer the possibility to measure (also) with CVS.
- Nucleation mode should be measured if a dilution setup, where it can be measured reliably and reproducibly, can be found. This setup is probably difficult to realise but thorough investigation to find it should be done.

7.2. Instrumentation

It is clear that a wide variety of particle sizing instrumentation is available to characterise the particulate vehicle emissions. It is also notable, that particles have been reported over 4 orders of magnitude (1 nm – 10 µm), and thus it is unlikely that any single technique could offer a full characterisation of the particle mixture. This is particularly true on the basis that the physical attributes of the particle used to measure across this range changes from diffusion and mobility-based parameters to sedimentation and impaction based parameters. Thus a combination of instruments must be employed. In general, real- or near real-time instrumentation is preferred due to the dynamic nature of the measurements. Different instruments are summarised in the next table.

Table 6-1: Specifications of commercially available instruments.

Device	Type	Magnitude	Diameter	Range (µm)	Size Discrimination	Time Constant	Chemical information
MOUDI	Impactor	Mass	Aerodynamic	0,056-10	10 Stages	~min	With mass analysis
Andersen MkII	Impactor	Mass	Aerodynamic	0,4-6,5	7 Stages	~min	With mass analysis
Hauke LPI25	Impactor	Mass	Aerodynamic	0,015-16	11 Stages	~min	With mass analysis
QCM	Impactor	Mass	Aerodynamic	0,05-25	10 Stages	1 s	With mass analysis
TEOM	Filter	Mass	-	PM	-	1 s	-
EAA	Electrost. Classifier	Size & Number	Mobility	0,01-1	9 Classes	~3min	-
DMPS	Electrost. Classifier	Size & Number	Mobility	0,01-1	43 Classes	~20min	-
SMPS	Electrost. Classifier	Size & Number	Mobility	0,007-0,7	~nm	2-3min	-
ATOFMS	APS+Spectroscopy	Size & Speciation	Aerodynamic	0,4-50	~µm	600 part/min	Spectroscopy
OLTFMS	APS+Spectroscopy	Size & Speciation	Aerodynamic	0,4-5	~µm	600 part/min	Spectroscopy
TEM	Microscope	2D Size and Shape	Geometric, Fractal	0,001 -1	~nm	h	-
SEM	Microscope	3D Size and Shape	Geometric, Fractal	0,01-50	~nm	h	-
NanoMet	Combination	Size, species	Aerodynamic / Mobility	0,015-0,19	4 Stages	s (one size) - min (4 sizes)	Discrimination volatiles / condensables, species (calibration required)
ELPI	Impactor	Size and number	Aerodynamic	0,03-7	12 Stages	1 s	With mass analysis

7.2.1. Particle Sizing

Particle sizing techniques required to characterise the particle size range must also be considered with respect to the time-base of the measurement. Thus measurement techniques can be considered with respect to steady-state or transient measurements.

The SMPS, operating in the range from 7-300 nm, or 15 – 700 nm, yields information about number-based distributions over most of the particle size range of interest. However, the SMPS cannot be used for transient measurements. A number of SMPS instruments, with the Electrostatic Classifier set to monitor particle concentrations at fixed size points, have been used to monitor number concentrations across transient cycles. Alternatively, the measurement cycle can be repeated with different classifier settings to produce the size distribution. These methods are expensive, if not impractical, for a large-scale study.

The ELPI offers near real-time size distribution information. Recently, the measurement range has been extended to approximately 10nm. This could be just enough to measure the nucleation mode, but there is no experience of this set-up yet. There are also reliability issues relating to particle bounce and particle density.

In the future, the NanoMet can offer an interesting alternative for real-time size distribution measurement, but the sizing system is still under development.

Recommendations:

- For steady-state measurements, the obvious instrument of choice is the SMPS.
- For transient cycles, ELPI should be tested. A CPC or size locked SMPS should be used in parallel, if possible. In addition, steady state measurement comparison with SMPS is advisable.

7.2.2. Integral concentration measurement

Particle mass should be measured with the regulated method for legislation, comparison and continuity purposes. Real-time mass measurement has most readily been achieved using TEOM technologies. It should also be noted that this type of technology (with very high mass sensitivity) may be required for future regulated measurements as mass outputs from engines decrease toward the effective detection limits of gravimetric methods. It is noted, however, that these are prone to uncertainties from collection and subsequent evaporation of water and volatile species.

In general, Condensation Particle Counter (CPC) technology has proven robust, accurate and reproducible in measuring particle number concentrations in real-time. It should be noted, however, that of the commercial instruments available, there are differences in sensitivity and limit of detection for the smallest particles, and hence care is required in defining a lower size cut-point.

Surface area techniques are less well defined in vehicle emissions measurement, although they are of increasing interest due to toxicology data suggesting that available surface area is one of the critical parameters in assessing relative toxicity. In general, the available techniques are unproven in this application, but the diffusion charger appears to offer scope for reproducible measurement. This instrument is relatively inexpensive. It should be noted that if ELPI is available the total measured current in the ELPI corresponds to diffusion charger signal.

Recommendation

- Standard gravimetric method for mass and CPC for number concentration
- TEOM should be tested for solid particles
- Diffusion charger should be tested due to additional information for relatively low cost.

7.2.3. Chemical composition

Chemical composition analysis for this project is discussed in the appendix 1. Sampling requirements need to be evaluated for each class of compound collected.

It may however be appropriate to monitor the concentration of nanoparticle precursors (SO_2 and hydrocarbons) as an indirect measure of the ‘nanoparticle formation potential’.

Appendix 1: Chemical analyses

SOLUBLE ORGANIC FRACTION

Definitions:

Particulate Matter (PM)

Particles formed by incomplete combustion of fuel. Compression ignition (diesel) engines generate significantly higher PM than emissions than spark ignited (gasoline) engines. The particles are composed of elemental carbon, heavy hydrocarbons and hydrated sulphuric acid.

Total Particulate Matter (TPM)

The total particulate matter emissions including all fractions of diesel particulates, i.e. the carbonaceous, organic and sulphate particulates.

Soluble Organic Fraction (SOF)

The organic fraction of diesel particulates. SOF includes heavy hydrocarbons derived from the fuel and the lubricating oil. The term “soluble” originates from the analytical method used to measure SOF which is based on extraction of particulate matter samples using organic solvents.

Volatile Organic Fraction (VOF)

The organic fraction of diesel particulate matter as determined by vacuum evaporation. It may or may not be equivalent to the SOF fraction. Depending on the exact analytical procedure, the VOF may include the organic material (SOF) as well as some of the sulphate particulates which, being composed primarily of hydrated sulphuric acid, are also volatile.

Sampling

With regard to regulatory particulate emissions, 70/220/EEC requires, inter alia, that the particulate sampling unit consists of a dilution tunnel, a sampling probe, a filter unit, a partial-flow pump, and a flow rate regulator and measuring unit. The particulate-sampling part flow is drawn through two series-mounted filters. The sampling probe for the test gas flow for particulates must be so arranged within the dilution tract that a representative sample gas flow can be taken from the homogeneous air/exhaust mixture and an air/exhaust gas mixture temperature of 325 K (52°C) is not exceeded. In the USA, 40 CFR, Part 86 has the same requirement. The requirements for filter pre- and post-conditioning are also clearly defined.

Typical industry standard filters are constructed from borosilicate microfibres reinforced with woven glass cloth and bonded with PTFE. This construction allows folding for weighing and offers low air resistance and high filtration efficiency. The maximum operating temperature in air is 260°C. Higher temperature operation (up to 1100°C) is possible with pure quartz filters.

SOF determination

The authors of EPA/600/8-90/057D, a draft Health Assessment Document for Diesel Emissions (Nov. 1999) comment that, "Diesel exhaust particles are aggregates of primary spherical particles consisting of solid carbonaceous material and ash, and which contain adsorbed organic and sulphur compounds (sulphate) combined with other condensed material. The organic material includes unburned fuel, lube oil, and partial combustion and pyrolysis products. This is frequently quantified as the soluble organic fraction, or SOF. The SOF can range from less than 10% to more than 90% by mass, with the highest values occurring at light engine load where exhaust temperature is low (Kittelson, 1998). The SOF fraction can also vary with engine design, with high lube oil emitting products producing higher SOF. Sulphate depends on fuel sulphur content primarily.

Carbonaceous diesel particulate matter has a high specific area (30-50 m2g-1) (Frey and Corn, 1967). Because of this high surface area diesel particles are able to adsorb large quantities of organic materials. After removal of the organic material by extraction, the surface area increases to as high as 90 m2g-1 (Pierson and Brachaczek, 1976). A variety of solvents have been used to extract the SOF (Levson, 1988). Soxhlet extraction with a binary solvent consisting of an aromatic and an alcohol appears to give the best recovery of PAH's, although dichloromethane is also used. Some studies have then used liquid chromatography to separate the extract into various fractions on the basis of chemical composition and polarity."

Paul Williams (University of Leeds, UK) suggests three major methods of determining SOF. Each method is briefly outlined below, together with its perceived advantages and disadvantages:

Soxhlet Extraction

Method

- Weigh filter at controlled temperature and humidity
- Soxhlet extraction with organic solvent, e.g. methylene chloride, for 8 hours
- Remove filter – allow solvent to evaporate
- Weigh filter at controlled temperature and humidity

Advantages

- Non destructive
- Allows further analysis of the SOF
- Inexpensive

Disadvantages

- Time consuming

Vacuum oven sublimation

Method

- Weigh filter at controlled temperature and humidity

- Vacuum oven sublimation; 200°C for 18-24 hours
- Weigh filter at controlled temperature and humidity

Advantages

- Simple
- Multiple filters
- Comparable with Soxhlet extraction

Disadvantages

- Destructive
- Possible errors (see below) – also, more sulphate removed than Soxhlet extraction.

Improvements to overcome possible errors

- Vacuum pump oil backstreaming can be prevented using an activated carbon trap
- The oven door should be fitted with a temperature stable seal
- Desorption of hydrocarbons from previous analyses can be prevented by using a continuous nitrogen purge

TGA

Method

- Filter placed on micro-balance
- Filter heated in inert gas
- Weight loss monitored directly with temperature

Advantages

- Simple
- Direct measurement of weight loss
- Eliminates "oven" problems

Disadvantages

- Expensive
- Destructive
- Sulphate still a problem

In general terms, the vacuum sublimation and TGA methods have been developed to try and mimic Soxhlet extraction, which remains the industry standard (Williams, private communication, May 2000). The main difference is that the thermal techniques tend to remove most of the sulphate as well as the SOF, and Soxhlet extraction to leave most of the sulphate. However, if the PARTICULATES programme is solely concerned with knowing the carbonaceous content of the particulates produced, or is using low sulphur fuel, then the thermal methods may still be appropriate.

Diane Hall (BP) has noted that, “the measurement of volatile material on Diesel particulate trapped on filter papers has been addressed by a group within the UK Institute of Petroleum (IP). The role of the IP is to prepare standard test methods for application to issues related to petroleum products and IP ST-G-10 addresses the analysis of unregulated automotive emissions. This group is attended by members of both oil and motor industries and also third party contract labs and has representatives from all over Europe (some 30 people). The methods produced from the group are the result of several years of round robin experimentation and statistical analysis.

There are already two standard methods available for the analysis of organic material (fuel/lube):

- IP 442/99 - analysis of fuel and oil derived hydrocarbons in Diesel particulate on filters (GC method).
- IP 443/99 - extraction of SOF from Diesel particulate on filters (Soxhlet method).”

The principle employed in IP 443 is that the filter, or portion of the filter, is placed in a Soxhlet extraction apparatus and extracted with dichloromethane. The dichloromethane extract is placed in an evaporator and the extract reduced to between 1 ml and 2 ml. The concentrated extract is then taken up in carbon disulphide, placed in a sealed container and stored at below 5°C prior to analysis. This analysis could be by the gas chromatography method described in IP 442. Annex A of IP 443 gives a procedure for the gravimetric determination of SOF by the weighing of an appropriately conditioned filter, soxhlet extraction, drying, reconditioning and reweighing. The results are compared with those of a blank filter.

Both Soxhlet extraction and TGA methods were employed by ACEA (ACEA report on small particle emissions from passenger cars – December 1999). Samples were collected in parallel on Teflon-coated filters for Soxhlet extraction using cyclohexane and on glass fibre filters for TGA analysis. The evaporation curves generated during heating of the particulate matter in nitrogen on the TGA could be compared with those for fuel, oil and sulphuric acid. The temperatures corresponding to 95% evaporation were approximately 250°C for fuel, 400°C for sulphuric acid and 450°C for oil.

HYDROCARBON ANALYSIS

IP 442/99 describes a standard method for the analysis of fuel and oil derived hydrocarbons in diesel particulate collected on filters, in the sub-milligram to milligram range. It is applicable for the analysis of filters as received and of the soluble organic fraction extracted from the filter. Either a portion of the filter is taken and the hydrocarbons are thermally desorbed or an aliquot of the extracted material is injected onto a capillary column in a gas chromatograph, and quantified by comparison with analyses of oil and topped fuel standards.

PAH ANALYSIS (SU)

Particulate size fractions

Sampling

When size fractionated particulate sampling was performed for chemical analysis the inlet tubing was mounted directly to a ELPI impactor. Each impactor stage is supplied with a chemically inert fibreglass filter disc (Whatman GF/C) used as substrate. The particulate mass for each impactor stage was obtained by weighing the substrate filters prior to and after sampling with a microbalance (rated precision 1µg). After sampling, the filters are stored at -18°C until extraction.

Extraction

Each individual particle size fraction was extracted with 5ml of dichloromethane for 30min using an ultrasonic bath. This procedure was repeated twice which showed that more than 97% of PAH had been extracted using 5ml DCM for 30min with two repeats. Blank particle size fraction samples were obtained and treated as described above. The crude DCM extract was stored at -18°C until chemical analysis.

Chemical fractionation

The particulate size crude extracts are normally fractionated accordingly to polarity into five fractions before chemical analysis. Five fractions are collected containing:

➢ fraction I:	"light" aliphatic hydrocarbons,
➢ fraction II:	"heavy" aliphatic hydrocarbons and PAH,
➢ fraction III:	nitro-PAH,
➢ fraction IV:	dinitro-PAH and quinones,
➢ fraction V:	polar material.

The procedure followed the one described by Alsberg et al. (2).

Particulate phase associated compounds

Sampling

The particulate sampling was performed in accordance to the US Federal Test Procedure (FTP) using Pallflex T60A20 (250mm diameter) filters. Before sampling, the filters were washed with ethanol, acetone and DCM and dried at 200 C; this cleaning procedure is described elsewhere (1). After sampling, the filters were stored at -18°C until extraction.

Extraction

The filters were Soxhlet extracted with DCM for 18h. The DCM extract was evaporated under reduced pressure to just dryness, diluted with acetone and then stored at -18°C until chemical analysis. Blank samples were obtained and treated as described above.

Chemical fractionation

The crude extracts from the conventional filter used for the collection of particulate emission samples are fractionated into fraction I (not further analysed) and fraction II which was analysed for PAH, as described below, in selected ion monitoring (SIM) mode. Internal standards were added to the raw particulate extracts.

PAH analysis

Fraction II emanating from each particle size fraction are analyzed using gas chromatography-mass spectrometry (GC-MS) for the characterization and identification of the compounds present. The gas chromatograph (Hewlett Packard 5890 series II) was equipped with a split/splitless injector (injector temperature 285°C) and a fused-silica capillary column (20m x 0.25mm i.d., HP5-MS, Hewlett-Packard, USA). The temperature program was as follows: Initial temperature 70°C for

1min, rate 7°C/min, final temperature 300°C for 10min. The mass selective detector (Hewlett Packard 5971A) interface temperature was set to 300°C and the ion source temperature approximately 200°C. The MS is operated in the Electron Impact (E.I.) mode at 70eV. Specific analysis of PAH in fraction II is carried out using the above GC-MS set up and the quantitative analysis are carried out in the Selected Ion Monitoring (SIM) mode.

Prior to the chemical fractionation and the SIM analysis of fraction II, internal standards were added, i.e. d10-phenanthrene and 2,2'-binaphthyl. A PAH standard mixture with internal standards was used for the determination of retention times and response factor calculations.

References

1. Westerholm R. Almén J., Hang L., Rannug U., Egebäck K-E. and Grägg K. (1991) Chemical and biological characterization of particulate, semi-volatile and gas phase associated compounds in diluted heavy duty diesel exhausts: A comparison of three different semi-volatile phase samplers. Environ. Sci. Tech. Vol. 25, 332-338.

2. Alsberg T., Stenberg U., Westerholm R., Strandell M., Rannug U., Sundvall A., Romert L., Bernsson V., Petterson B., Toftgård R., Franzen B. Jansson M., Gustafsson J-Å. Egebäck K-E. and Tejle G. (1985) Chemical and biological characterization of organic material from gasoline exhaust particles. Environ. Sci. Technol. Vol. 19, 43-50.

ANIONS (AEAT)

Anions are determined using the technique of Ion Chromatography (IC). Samples are prepared for analysis by extracting the filter papers with 10% solution of iso-propanol in anion-free water (in accordance with the Institute of Petroleum method BT/94; now IP416/96, Determination of sulphate and nitrate in dieesl particulate filter samples). To reduce the ‘blank’ levels, the papers are pre-extracted prior to use. IC is then used to separate the individual anions, whose peak heights and retention times are compared to those of standards to obtain quantitative data. The cyclade wash solutions are similarly treated.

It should be noted that although the Limits of Detection (LOD) for the anions measured are approximately 0.1 µg per ml, the volume of sample affects the concentration at which a ‘less than’ figure is reported. This is particularly relevant for the cyclade washes, since whilst it is possible to detect 0.1 µg of analyte in 1 ml of solution, the same weight in 20 ml of cyclade washings would be undetectable and a LOD of <2 µg would therefore be reported.

The technique is based on that used for the measurement of anions in rainwater. This is within AEA Technology’s NAMAS accreditation schedule. The uncertainty of the results given by the technique is estimated to be 10%.

Evaluation

It is considered that the IC technique is reliable for the reproducible determination of trace amounts of anions. However automotive samples can contain very low levels of anions, and these levels can be close to or equal to the levels found on the ‘blank’ filters.

ACIDITY (AEAT)

The acidity of particulates can be measured by the modified ‘Granplot’ technique. The samples are extracted with a solution of 10% iso-propanol in 10-4 M HCl containing a small amount of NaCl. The pH of the resulting solution is measured using a sensitive electrode and the extract titrated against small aliquots of very dilute alkali solution, the pH being measured after each addition. A plot of the volume of alkali added against the ‘Gran function’, related to the pH, is then made and extrapolated to meet the function axis. This gives the total acidity; the acidity of the sample is then calculated by subtracting the acidity equivalent of the extracting solution.

Evaluation

In past tests, a Euro I engine gave only moderately satisfactory results with regard to repeatability. It was not possible to obtain a result from the small amount of particulate sample collected from a pilot vehicle (IDI turbo-charged diesel). A null result was obtained for a gasoline vehicle. Acidity results are prone to uncertainty since particle acidity (largely resulting from sulphur in diesel) can be modified by neutralisation reactions in the exhaust, on the filter paper or during extraction. It is quite likely that a significant proportion of the potential sulphate acidity is neutralised by metals in the exhaust gas, emitted initially as metal oxides.

The majority of the measurable ‘strong’ acidity is expected to be associated with sulphuric acid. There could be additional ‘weak’ acidity associated with organic surface groups on the particulates, but these are probably not measured in a Gran titration which is a method specific to strong’ acids.

METALS BY ICP (AEAT)

Two techniques are used to analyse for metals: Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Inductively Coupled Plasma Atomic Emissions Spectrometry (ICP-AES). ICP-AES is the most widely used technique, but for increased sensitivity, and in cases where no suitable emissions lines exist, ICP-MS is used.

Prior to measurement, for both techniques, the samples are prepared to a form suitable for analysis. The filter media is ashed at 550°C and the residues dissolved by refluxing with concentrated HCl/HNO3 for 3 hours. After concentration to 1 ml, the samples are diluted to 10 ml with de-ionised water and analysed. The cyclade washes are evaporated and similarly treated.

ICP-MS

This is a multi-element analytical technique ideally suited to the determination of the concentrations of elements or isotopic ratios in aqueous solutions. A radio-frequency inductively coupled plasma is used to produce singly-charged ions, at atmospheric pressure, from the nebulised sample solution. These ions are then extracted into an evacuated chamber where they are separated, according to their mass, using a quadrapole mass spectrometer. The ions are detected using an electron multiplier. Elemental concentrations are then calculated by reference to standards taken through the same procedure. Although technically sequential, the mass spectrum is scanned at a high enough rate to make it appear that the technique gives a simultaneous determination of all the analytes present.

This technique is within AEA Technology’s NAMAS accreditation schedule. The accuracy of the technique is quoted as 10%.

ICP-AES

This is another multi-element analytical technique for the determination of the concentrations of elements in aqueous solutions. A radio-frequency inductively coupled plasma is used to excite the atomic emission spectra of elements present in the nebulised sample solution. This radiation is analysed with a vacuum spectrometer and selected wavelengths are detected with photomultiplier tubes. Elemental concentrations are then calculated by reference to standards taken through the same procedure. Up to 45 elements may be determined simultaneously with this technique.

This technique is also within AEA Technology's NAMAS accreditation schedule. Quality control standards are analysed with each batch of samples and the results obtained are in excellent agreement with those expected. The accuracy of the technique is quoted as 10%.

Evaluation

It is considered that both of the above techniques are reliable for the reproducible determination of trace metals with an accuracy of 10%. However, the samples can contain very low levels of the analytes sought, and these levels can be close to or equal to the levels found on the 'blank filters'.

METALS BY NEUTRON ACTIVATION ANALYSIS (JRC)

Neutron activation analysis is a powerful tool to determine a great variety of elements in environmental, biological and geological samples. By neutron capture, a compound nucleus is formed in an excited state, which decays almost instantaneously to the ground state, by gamma-ray emission. The gamma-ray spectrum is a fingerprint of the element. However, for some elements neutron capture results in the formation of either stable isotopes or gamma-ray emitting isotopes with inadequate half-life and source strength. For these elements, the prompt gamma-ray spectrum emitted after neutron capture can be used for the determination of the element composition of a sample. In this analysis two main nuclear techniques will be employed, namely neutron activation and prompt gamma analysis, backed-up by a number of conventional techniques for comparison purposes.