ACEA Programme on the Emissions of Fine Particulates from Passenger Cars (2)

Part 2: Effect of Sampling Conditions and Fuel Sulphur Content on the Particle Emission**Martin Mohr, Urs Lehmann**

Swiss federal Laboratories for Research and Materials Testing (EMPA), Dübendorf, Switzerland

Giovanni Margaria
ACEA^o

Copyright © 2003 Society of Automotive Engineers of Japan, Inc.

ABSTRACT

The results of an investigation of the influence of the sulphur fuel content and different dilution techniques on fine particulate emissions are reported in this paper. Fuels with two different sulphur contents (<10 ppm and approx. 200 ppm) were used for a Diesel and a gasoline vehicle in order to compare four different dilution procedures. These comprised the standard CVS tunnel and two pre-heated and one non-heated direct dilution systems. Various particulate measurement instruments were employed simultaneously, including SMPS, CPC, and ELPI for number and size, the standard gravimetric filter method for mass. In addition, Soxhlet extraction for chemical composition was carried out.

A higher fuel sulphur content was found to clearly increase particulate emissions from the Diesel and the gasoline vehicle for higher load. The increase in emissions was due to the contribution of condensed material and most of it could be clearly brought into relation with to sulphur compounds. The comparison between the different dilution systems showed a good agreement for the accumulation mode in number and size. Drastic differences were observed concerning the nucleation mode for the tests with high sulphur fuel. Whereas the pre-heated dilution systems do not show a nucleation at all, the total number concentration was increased up to an order of magnitude for the non-heated systems.

INTRODUCTION

Until now particulate emissions have been regulated and limited in emissions and ambient air quality particle legislation through particulate mass. The measurement methodology employed for vehicle emissions is gravimetric, which involves collecting particles under prescribed conditions on a filter and weighing. This methodology has been fulfilled the

demands in a very reproducible and reliable way. In 2005 the particle emissions limit for new European passenger cars will decrease to 0.025 g/km and Diesel cars equipped with a trap will result in even lower concentration. As the impact of small particles on human health is receiving increasingly intense scrutiny [1], interest has grown in examining other parameters such as particle size and number. For this reason, new methods are discussed to complete or replace the present methodology for legislation. The European Commission is required to take into account improvements in the test procedures for small particles in any future legislation for entry into force after 2005 (Article 3, 98/69/EC). One major activity that reviews advanced particle measurement methodologies is the Particle Measurement Programme (PMP) under the auspices of the UN-ECE working group GRPE. In contrast to gravimetric measurements, there is not yet a standardised method that fulfils the many requirements demanded for certification testing. As a result studies on particle number emission revealed large differences in the results due to the use of different sampling and dilution procedure and measurement principles. The situation is aggravated when fuel with non-minimised sulphur content is applied.

In this paper we present results of the 2nd ACEA programme on fine particle emissions from passenger cars in 2002 [2], which is a follow-up of the first ACEA particle programme [3]. The programme in 2002 comprised two objectives: the comparison of particle emissions of an extended range of engine technologies and the comparison of different dilution and particle measurement techniques and to examine the influence of the sulphur fuel content on the emissions. The results of the first subject are presented in [4]. This paper deals with the second subject. Four different dilution procedures were compared for a Diesel and a gasoline passenger car each running with fuels of two different sulphur

contents. The particles were characterised in number, size and composition and related to the regulated mass measurement method.

BACKGROUND PARTICLE FORMATION

Soot is formed during combustion in locally rich region in the combustion chamber [5]. Although the majority of the primary particles are burned again inside the chamber, a high number concentration is still left before the outlet of the combustion chamber that causes sudden agglomeration. Carbonaceous material proves to be the dominant fraction of solid particles, as the ash condensation of metal compounds in the lubricant is rather low for today's internal combustion four stroke engines. The solid carbonaceous particles in the exhaust gas consist of highly agglomerated and are generally referred to as accumulation mode particles (**Figure 1**). During the cooling in the exhaust system, condensation processes take place. Vapour of products of incomplete combustion condenses on the existing particles and new, volatile droplets can be formed. In addition, droplets may be formed by condensation during the sampling and dilution. The formation of new volatile droplets depends on the amount of the gaseous species and solid particles [6, 7], the temperature and the dilution conditions after tail-pipe emission. The sulphur in the fuel is considered to be a main source of volatile droplets. It is assumed that nucleation particles mainly consist of volatile sulphur-and/or hydrocarbon compounds (e.g. sulphuric acid) [8]. The presence of the droplets can be usually recognised by a separated mode (called nucleation

(CPC3022A, TSI, USA) and an electrical low-pressure impactor (ELPI, DEKATI, Finland) [9]. In addition, ELPI is able to measure the number size distributions in transient and steady state tests. For ELPI the seven lower stages were evaluated covering a size range between 35 nm and 1 μm . Scanning Mobility Particle Sizers (SMPS 3934, TSI, USA) [10, 11] were applied for detailed number size distributions in the size range between 11 nm and 514 nm for steady state tests. It has to be mentioned that the aerodynamic-equivalent diameter is measured by ELPI, whereas the electrical mobility equivalent diameter is determined by SMPS. As particle density affects the results of ELPI, they are not directly comparable to the SMPS data. Particulate Matter (PM) of the exhaust gas is determined gravimetrically according to the regulations [70/220/EEC]. The chemical composition of the particulate matter (PM) was determined by extraction of the gravimetric filter samples in a Soxhlet apparatus. By two subsequent extractions, the filter loading can be divided in a soluble organic fraction, a soluble inorganic fraction and non-soluble fraction. By ion chromatography analysis of the soluble inorganic fraction, the amount of sulphate ions is determined.

A thermodesorber was used to distinguish between solid and volatile particles. In this study the thermodesorber was controlled to a temperature of 350°C [12]. The residence time in the heated tube was about 1.8 s. All SMPS/CPC measurements were carried out simultaneously with and without TD. The losses of solid particles of about 25% were corrected in the results. More details of the particle measurement instruments are described in the first paper about this measurement programme [4].

Figure 1: Typical number size distribution for particles with nucleation and accumulation mode.

mode) in the number size distribution (**Figure 1**).

EXPERIMENTAL

INSTRUMENTATION

Particle measurement instruments

Particle emission was characterised by number, size, mass and composition. The total number emissions were measured using condensation particle counters

Dilution systems

CVS-System

Two completely separated sampling lines were used for the exhaust of the Diesel and gasoline vehicle, consisting of the full flow constant volume sampler (CVS) tunnel and a partly heated tube (80 °C) that connects the exhaust pipe of the vehicles to the tunnel. A minimum dilution ratio of 10 was used for all operation conditions. For particle number measurements a separate probe was installed close to the probe for the gravimetric filter sampling. In order to achieve a higher dilution ratio for the number measurements, an additional ejector-type diluter unit with a constant dilution factor of about 10 was installed downstream of the CVS for particle number measurements.

Ejector-type dilution unit

The ejector-type dilution unit consists of an inlet nozzle, an annular nozzle and a mixing chamber [13]. Inside this system particle-free pressurised air (dilution air) is mixed with the aerosol sample. A pressure drop at the ejector nozzle achieves a homogeneous mixing and constant dilution ratio. As the

dilution ratio of ejector-type dilution units depends on the pressure drop across the nozzle and the temperature of the gases all dilution units were calibrated by CO₂ concentration measurements before the measurement programme. The actual dilution ratio was determined by measuring the pressure drop based on the calibration or directly by simultaneous measurement of CO₂ concentration up- and downstream of the dilution system during the tests. For measurements without CVS the ejector dilution system was used in a double stage configuration consisting of two ejector-type dilutions units (**Figure 2**). In this case, a residence tube was placed between the two ejectors with a calculated residence time of 2 seconds. The dilution ratio of the total system was about 100. The system was installed as close to the exhaust pipe as possible. The transfer line between the exhaust pipe and the dilution unit was always heated up to 110°C. For the measurements entitled with «Ej. cold» the ejector and the dilution air were not heated. For the measurements entitled with «Ej. hot» the first ejector and the dilution air were controlled to a temperature

Figure 2: Sampling and dilution system using two ejectors

of 80°C. The second ejector dilution unit was operated always at room temperature.

Rotating disk dilution unit

The principle of the rotating disk dilution unit (MD19-1e, Matter Engineering AG, Switzerland) is based on the transport of small discrete aerosol portions from raw aerosol stream to a particle-free gas stream, the sample flow. A schematic is shown in **Figure 3**. The exchange of the volumes is done by small cavities engraved on a rotating disk that has contact to both channels [14]. The dilution ratio is determined for fixed cavities by the rotating speed and the sample flow. This method accomplishes dilution of aerosol in a wide dilution range. The dilution ratio of the system

Figure 3: Sampling and dilution system using a rotating disk

was controlled to about 100 for this programme. The actual dilution ratio was determined by gas concentration measurements before and after the tests. The transfer line between the exhaust pipe and the dilution unit was always heated up to 110°C. The rotating disk dilution unit was set to a temperature of 80°C. Due to the low sample flow through the rotating disk dilution unit ELPI measurements were not carried out for this configuration.

COMPLETE EXPERIMENTAL SET-UP

Figure 4 shows the complete set-up for the measurements. Four different dilution procedures were applied for the fine particle measurements: the full flow CVS dilution tunnel followed by an external ejector dilution unit (CVS), a double stage ejector based dilution unit at heated (Ej hot), and non-heated operation (Ej cold) and a rotating disk dilution unit (Rotating disk). The aerosol sample was carefully distributed to the 3 CPC's, the two SMPS and to the ELPI as can be seen in the schematic from the set-up.

vehicle code	Ref	Diesel	Gasoline
Inertia Mass [kg]	1470	1590	1020
Transm (M5, A5)	M5	M5	M5
Displacement [ccm]	1910	1896	1242
No of Cylinders	4	4	4
Valves per Cylinder	2	2	4
Max Power [kW]	81	74	55
Max Torque [Nm]	275	240	110
Compression ratio	18.45	19.5	10
Combustion Type	Diesel DI	Diesel DI	SI
Injection Type	C-Rail	Mech	MPI
EGR Type	Electr Closed Loop	Electr Closed Loop	none
Emis Control Type	Oxy	Oxy	3W

Table 1: Technical data of the cars tested in the ACEA PM Programme 2

Figure 4: Schematic set-up of the programme

TEST VEHICLES

The measurement programme was run with a Diesel and a gasoline passenger car. The Diesel vehicle was a modern turbo-charged VW Bora TDI. The gasoline vehicle was a Ford Fiesta, naturally aspirated with multi-point port injection (MPI). Both vehicles were certified according Euro 3 legislation. In addition another modern Diesel vehicle (Alfa Romeo 1.9 JTD) was used for reference tests. More details of the vehicles are given in Table 1.

FUELS AND LUBRICANTS

All tests were run with so-called sulphur-free fuels, i.e. with less than 10 ppm sulphur and high sulphur fuel, S = 246 ppm for Diesel, S = 175 ppm for gasoline. The high sulphur gasoline fuel was produced by doping fuel from the sulphur-free fuel batch by addition of sulphur compounds. As doped

Diesel fuel could not be obtained two different fuels had to be used, resulting in not identical properties. All vehicles were driven with the same commercially available high-quality lubricant. Details of the specification of the lubricant oil and the fuels are given in Table 2 and Table 3.

Density @ 15°C	854.6	kg/m ³
Sulphur	4760	mg/kg
viscosity at 40°C	81.34	mm ² /s
viscosity at 100°C	14.19	mm ² /s
sodium	7	mg/kg
magnesium	1100	mg/kg
phosphor	860	mg/kg
zinc	1000	mg/kg
chlorine	0.9	% wt

Table 2: Specification of lubricant oil

		Diesel fuels		Gasoline fuels	
		D 210 F 50	D 236 F 53	CEC-RF-02-99	CEC-RF-02
Density @ 15°C	kg/m ³	822.1	827.2	750.5	750.9
Sulphur	mg/kg	< 10	246	< 10	175
Aromatics	% wt	20.8	21.9	37.5	37.5
Saturates	% wt	79.2	78.1		
Benzene	% wt			0.16	0.16
10/50/70/95% rec.	°C	216/243/259/294	193/253/290/364	54/101/116/186	54/101/117/185

Table 3: Specification of the fuels

MEASUREMENT PROGRAMME

TEST PROTOCOL

The Diesel vehicle and the gasoline vehicle were measured during a transient cycle (NEDC2000) and three steady state modes (120 km/h, 100 km/h, 50 km/h). The transient tests were repeated two times whereas the steady state modes were run only once. The tests were repeated using four different sampling procedures and two different fuel qualities. All cars were conditioned exactly in the same way. The conditioning for the transient tests were carried out according to the regulations. For the steady state tests the vehicles were warmed up to ensure stable conditions. This was checked by monitoring the lube oil temperature and the exhaust gas temperature. In advance of the testing, they were run for a distance of at least 500 km with the same fuel and lubricant used in the official programme. Before doing the tests using the high sulphur fuel the vehicles were also conditioned for 500 km with the new fuel. **Table 4** gives an overview of the test programme.

Vehicles	1 Diesel vehicle, DI 1 port injected gasoline vehicle
Fuels	Diesel (S< 10 ppm), Gasoline (S<10 ppm) Diesel (S= 250 ppm), Gasoline (S=175 ppm)
Cycles	NEDC2000 (cold start: +23°C) Steady state: 120 km/h (5. gear), 100 km/h (5. gear), 50 km/h (4. gear)
Measurement instruments	CPC DMA+CPC (SMPS) ELPI Gravimetric analysis
Chemical analytic technique	Soxhlet extraction
Sampling systems	Combination of CVS and ejector dilution unit Double stage ejector dilution unit (1. Stage heated) Double stage ejector dilution unit (1. Stage cold) Rotating disk dilution unit

Table 4: Overview of the test programme

Quality control

To ensure the comparability between the tests an extended cross-validation of the measurement instruments and additional runs were carried out weekly with a reference vehicle during the whole period (4 months) of the measurement programme.

Tests with artificial particle source

Tests with an atomiser, operating with a NaCl-solution, were performed to check the correct functioning of the CPCs and SMPSs instrument independent of the vehicle emissions. These tests give good information about the relative drift of the instruments with respect to each other. However, due to the very poor repeatability and stability the atomiser cannot be used for absolute reference for the calibration of the instruments. It should be mentioned that the ELPI is not suitable for salt aerosols due to strong bouncing effects. As can be seen in **Figure 5** there was no systematic drift of any instrument. With a few exceptions the scattering is within the accuracy of the instruments.

Figure 5: Test with artificial particles for comparing the instruments

Tests with reference vehicle

Once a week a measurement with the reference vehicle and low sulphur fuel was performed at constant speed 100 km/h to give a technical check of the whole experimental set-up.

The emissions of NO_x and PM show a relatively stable course of the measurements over this long time period (**Figure 6**). In contrast to that, all particle number instruments show a similar decrease of about 35% in the concentration during the period of 4 months of this programme (**Figure 6**). No cause in engine performance, exhaust pollutants or ambient conditions was found for this finding. The fact that all fine particle measurement instruments show the same trend suggest the involvement of the dilution system. Possible reason could be adsorption and desorption effects in the CVS tunnel depending on the vehicle measured before or creeping pollution of the ejector dilution system downstream of it, whose dilution ratio is very sensitive to pollution. However, no change in pressure drop over the nozzle was monitored during all the tests. In addition, the ejector and the nozzle were cleaned regularly during the whole programme. No final explanation can be given for the drift. Most measurements presented here are not affected by the effect. Only the concentrations of the measurements with the CVS set-up for high sulphur fuel (28.5.-1.6.) were corrected for the drift by multiply them by a factor 1.53.

Figure 6: Results for particle number, PM and NOx for the reference test

RESULTS AND DISCUSSION

The results for particle number measurements were corrected for the dilution factor, background concentration, diffusion losses in the sampling lines according to [15] and for losses inside the thermodesorber. Losses inside the dilution systems may be significant but were deliberately not corrected due to the high uncertainties. For tailpipe sampling the vehicle exhaust flow was determined by time-resolved measurement of the CVS flow and the dilution airflow in the tunnel. The results of gasoline vehicle were often very close to the detection limit. For this reason the observed results were less clear. The range bars shown in the diagrams indicate the maximum and minimum measured value out of 3 measurements. The measurements were carried out within a period of 13 weeks and some of the results that are compared to each other were in fact measured several weeks apart.

TRANSIENT TESTS

Figure 7 shows the effect of fuel on particle number and mass for the NEDC2000 test cycle. For the Diesel vehicle a increase in concentration was observed for particle number (+25%) as well as for particle mass (+8%) for higher sulphur fuel content. For the gasoline vehicle a significant increase was observed only for the particle number measured by CPC. This indicates a higher number of very small particles, as the ELPI do not show a similar effect. CPC measurements with thermodesorber showed that these particles consist mainly of volatile

Figure 7: PM mass by gravimetric analysis (right scale) and total particle number measured by CPC and ELPI (left scale) for Diesel and gasoline vehicle for the NEDC2000 with high and low sulphur content in the fuel.

material. In general a larger scattering was observed for measurements with high sulphur content in the fuel.

Figure 8 shows the effect of sulphur content for different dilution systems for the Diesel vehicle. Measurements even without thermodesorber show only a slight effect for CVS and Ej. Cold using different sulphur content. Only in case of the gasoline vehicle a clear increase is observed for the CVS (**Figure 9**) For this configuration the conditions seem to be most favourable for condensation. Apart from the fuel effect the dilution systems show an acceptable agreement taking the interval between the measurements into account.

STEADY STATE TESTS

More detailed information on the influence of sulphur content in the fuel can be obtained by the steady state tests. **Figure 11** reveals the strong effect of the dilution procedure. At 120 km/h and high sulphur fuel a drastic higher number was observed for the Diesel vehicle when the samples

Figure 8: Total particle number (CPC measurements with/without TD) of gasoline vehicles in the NEDC2000 test comparing high and low sulphur fuel.

Figure 9: Total particle number (CPC with/without TD) of gasoline vehicles in the NEDC2000 test comparing high and low sulphur fuel.

were taken with the CVS or ejector cold sampling system. For both configurations, the total particle number shows about a factor 7 higher concentration compared to the other configurations. The increased particle concentrations are not measured downstream of the thermodesorber, which indicates that these particles mainly consist of volatile droplets. At 50 km/h no significant effect can be observed. Apparently no nucleation took place when the aerosol was diluted with hot dilution air (Ej. hot, rotating disk) avoiding the saturation of the relevant compounds. **Figure 10** shows the number concentrations for the gasoline vehicle running with high sulphur fuel for the three steady state modes. For the steady state tests the concentrations are even one order of magnitude lower than for the transient tests and show a large variation. Nevertheless, a very strong nucleation mode was observed for the gasoline vehicle for 120 km/h with the CVS system. As for the Diesel vehicle these particles

Figure 10: Comparison of dilution systems: Gasoline vehicle driven with high sulphur fuel at different steady state conditions measured by SMPS

consist of small highly volatile material, as they are not measured with thermodesorber and ELPI.

MASS MEASUREMENTS

The findings of gradual decrease in nucleation potential with decreasing speed are in good agreement to the mass measurements as shown in **Figure 12**. For the gravimetric filter measurements the sample was always taken out of the CVS tunnel. It can clearly be seen for the Diesel vehicle that caused by high sulphur fuel the emissions are doubled for 120 km/h, plus about 40% increased for 100 km/h and no changes took place for 50 km/h. For the gasoline vehicle the filter loading was very low (about 20 µg) compared to blank tests (about 5 µg), causing a large uncertainty of the absolute data shown in the graph. In fact, no clear effect of fuel specification was observed in mass emissions for the gasoline vehicle.

CHEMICAL ANALYSIS

In **Figure 14**, it can be clearly seen that the additional particulate matter, which was found for the fuel with high sulphur content, consists primarily of soluble material. The main part of this fraction consists of sulphate and most of the fraction "SINOF w/o SO_4^{2-} " is probably water, which is usually bound to sulphate in such conditions. A larger organic fraction is also observed. The results of the chemical analysis are consistent with the number measurements, which showed a large fraction of non-solid particles as well for high sulphur fuel. The clearly speed-related increase of the non-solid fraction is probably explained by higher exhaust gas temperature at higher speeds that results in a higher reactivity in the oxidation catalyst. For this reason the conversion rate of SO_2 into SO_3 on the catalyst is higher. Sulphur trioxide subsequently may form sulphuric acid and associate water molecules. By this way a formation of new particles and an additional loading on the filter sample is caused when saturation is reached in the gas phase. According to Khalek et al. [8], the sulphuric acid can act as the nucleus for HC

Figure 11: Influence of fuel sulphur content on total number using different dilution systems for Diesel vehicle at 120 km/h and 50 km/h steady state conditions, measured by CPC.

condensation. This assumption could explain the higher organic fraction of the sample as mentioned above.

Figure 12: Particulate Matter (sample from CVS-tunnel) from the Diesel and the gasoline vehicle driving at steady state conditions using high and low sulphur fuel. The four bars are the four repetitions at same condition.

Figure 14: Chemical analysis of gravimetric filter: Diesel vehicle driven in constant speed conditions with different sulphur content in the fuel.

NUMBER SIZE DISTRIBUTIONS

The number size distributions as measured by SMPS for the Diesel vehicle, driven at 100 km/h for high and low sulphur fuel, are shown in Figure 13. A very good agreement is observed for the different dilution configurations when low sulphur fuel was used. We like to stress that there is a time gap of up to several weeks between the measurements. For high sulphur fuel additional volatile particles were measured when the configuration with the cold ejector dilution unit was used. They formed a separate mode at a size below 20 nm. In addition,

Figure 13: Number size distribution for Diesel vehicle at constant speed of 100 km/h for different fuel sulphur content (top: S < 10 ppm, bottom S = 250 ppm)

the variation of the accumulation mode is significantly higher for conditions using higher sulphur fuel. However, the mode of the distributions does not shift for any configuration. The distribution measured using the rotating disk is slightly lower.

TIME-RESOLVED EMISSIONS

The time resolved total particle numbers of the Diesel vehicle, measured by CPC in the transient cycle NEDC2000 show a good agreement between the different dilution systems (Figure 15). Only

Figure 15: Time resolution of total particle number measured with different dilution systems for NEDC2000, Diesel driven with sulphur-free fuel, measured by CPC

during the EUDC part some differences can be noticed.

CORRELATION BETWEEN THE MEASUREMENT INSTRUMENTS

The correlation of the different particle measurement instruments is presented in **Figure 16** for the steady state tests with high and low sulphur fuel. As an example the data for the particle measurement instruments (CPC, SMPS, ELPI) and the gravimetric filter mass measurement (PM) is shown when the samples were taken from hot ejector dilution unit. For low sulphur fuel all three particle number instruments show a clear correlation with PM. It can be seen that the SMPS generally measured a lower concentration compared to the CPC. A possible explanation could be the diffusion losses inside the DMA. ELPI data is presented for aerodynamic diameter and for this reason not directly comparable as a conversion to Stokes diameter would also effect the number concentration [16, 17]. For the heated ejector dilution system there was not any nucleation effects.

Figure 16: Correlation between total number measured CPC, SMPS and ELPI and mass of particles for heated double stage ejector based dilution system.

Nevertheless an effect of sulphur fuel content on the correlation was observed. For high PM emissions the slope seems to be less steep indicating a higher density of the particles. This weak supposition could be explained by a more compact structure of the particles.

SUMMARY

Particle measurements were carried out on a Diesel and gasoline vehicle with fuel of two different sulphur content ($S < 10$ ppm (D, G) and $S = 250$ ppm (D), $S = 175$ ppm (G)) and four different dilution methods. The experiments revealed clear effects of the fuel and the dilution method in particle emissions for both vehicles in most vehicle operation modes.

- For the Diesel vehicle a higher fuel sulphur content was found to increase the mass emission at higher load. For number emissions similar results were only observed for the non-preheated dilution. Although the Diesel fuels differ also in other properties the results of the chemical analysis indicate a key position of the sulphur for the findings.
- For gasoline vehicle the emission were too low compared to the scattering to draw reliable conclusions. Nevertheless significantly higher numbers were measured for some configurations with high sulphur fuel.
- The increase in particle emission while operating with the fuel of higher sulphur content was due to the contribution of non-solid material. The chemical analysis of the filter samples revealed that a large fraction consists of sulphates. Measurements with a thermodesorber showed that the higher particle numbers are caused by additional volatile particles. No nucleation was found at any operation mode when the low sulphur fuel was used.
- The comparison between the different dilution systems (CVS, ejector-based, rotating disk) showed a good agreement for the accumulation mode in number and size. For the non-preheated dilution systems (CVS, cold ejector dilution unit) a strong formation of new particles was observed for the Diesel and gasoline vehicle (only for CVS) for higher speed (120 km/h), when the higher sulphur fuel was used. In such cases substantial differences were obtained between the different dilution systems.
- For low sulphur fuel, the repeatability of all instruments was satisfactory within a measurement phase of approximately one week. Number measurements and gravimetric analysis were found to be within about $\pm 5\%$. These values are related to the Diesel vehicle w/o trap and when no nucleation took place. In some other cases the variation were found to be much higher. For higher fuel sulphur content, poorer repeatability was generally observed for the particle number measurements.
- The long-term stability for the reference tests was not satisfactory over the duration of the programme. A decrease of about 35% in particulate number concentration was observed during the 4-month duration. As there is no indication that the effect is caused by the vehicle, it is assumed that the dilution system (CVS tunnel combined with ejector based dilution system) is responsible for decrease in spite of rigorous quality control of the programme.
- For the different measurement techniques (CPC, SMPS, ELPI), a clear correlation in most cases was observed. In general, significantly higher particle numbers were found for CPC alone compared to the calculated number from the NSD measured by SMPS. The finding could be caused by diffusion losses inside the DMA. The discrepancy between ELPI and CPC/SMPS

is not surprising as the measurement methods are based on different principles and no corrections (e.g. for density) were applied.

- A clear relationship between particulate mass and number for all cycles and vehicles was found for measurements with the same fuel. However, there are large uncertainties associated with low particulate mass or if high numbers of nucleation mode particles occur.
- Up to now there is no method for absolute number calibration for particle measurement instruments. Therefore, the absolute particle numbers measured in this study are only valid for comparison within this study.

CONCLUSIONS

The results of the study suggest that the sulphur in the fuel only has an effect on the non-solid fraction of the particle emissions. This finding can be concluded from number, mass and composition measurements that show a consistent picture when dilution method was similar. The sampling method and dilution parameters highly affect the agreement between the different measurement methods for the non-solid fraction. On the other hand the solid fraction is unaffected and rather stable for the sampling and dilution method.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the EMPA colleagues for their large efforts and the following individuals of the member companies of ACEA for their valuable support: F. Boggio FIAT Auto SpA, G. Campiglio FIAT Auto SpA, S. Carli VOLKSWAGEN AG, H. Hinrichs GM Europe, C. Hosier Ford Motor Company, T. Mayer Ford Motor Company, J.C. Monique PSA Peugeot Citroen, O. Piacenza Fiat Auto SpA, P. Rouveiolles Renault SA, L. Ryan VOLKSWAGEN AG, V. Scheer Ford Motor Company, P. Sorsche DaimlerChrysler, R. Vogt Ford Motor Company.

°ACEA is the Association of European Automobile Manufacturers

References

1. Peters A. et al., «Respiratory effects are associated with the number of ultrafine particles», *Am J. Respir. Crit. Care Med.*, 155, 1376-1383 (1997)
2. ACEA programme 2002, «ACEA Programme on Emissions of fine Particles from passenger cars [2]», ACEA Report, (2002)
3. ACEA programme 1999, «ACEA Programme on Emissions of fine Particles from passenger cars», ACEA Report, (1999)
4. ACEA Programme on Emissions of fine Particles from passenger cars, Part1: Particle Characterisation of a Wide Range of Engine Technologies, SAE technical paper 2003-00-0080
5. Kittelson D.B., 1998, «Engines and Nanoparticles: A Review», *J. Aerosol Sci.*, 29, 575-588 (1998)
6. Mohr M., Jaeger W., Boulouchos K., «Einfluss von Motorparametern auf die Partikelemission», *MTZ worldwide*, vol. 62, 9/2001.
7. Mohr M., Steffen D., Forss A.-M. «Particulate Emissions of Gasoline Vehicles and the Influence of the Sampling Procedure», SAE technical paper 2000-01-1137.
8. Khalek I., Kittelson D., Brear F. «Nanoparticle Growth During Dilution and Cooling of Diesel Exhaust: Experimental Investigation and Theoretical Assessment», SAE technical paper 2000-01-0515.
9. Keskinen J., Pietarinen K., Lehtimäki M. «Electrical Low Pressure Impactor», *J. Aerosol Sci.* 23, 353-360 (1992)
10. Knutson E. O., Whitby K.T. «Aerosol Classification by Electric Mobility: Apparatus, Theory, and Applications», *Aerosol Sci.*, 6, 443-451 (1975).
11. Wang S.C., Flagan R.C., «Scanning Electrical Mobility Spectrometer», *Aerosol Science and Technology*, Vol. 13, 230-240 (1990)
12. Burtscher H. et al., 2001, «Separation of volatile and non-volatile aerosol fractions by thermodesorption: instrumental development and applications», *J. Aerosol Sci.*, 32, 427-442 (2001).
13. Koch W., Lödding H., Mölter W., Munzinger F., «Dilution systems for aerosol measurements with optical-particle counter at very high-concentrations», *Staub-Reinhaltung der Luft* 48 (9): pp. 341-344 (1988)
14. Hueglin Ch., Scherrer L., Burtscher H. «An Accurate, Continuously Adjustable Dilution System (1:10 to 10⁴) for Submicron Aerosols», *J. Aerosol Sci.*, Vol. 28, No. 6, pp. 1049-1055 (1997)
15. Willeke K., Baron A., 1993, «Aerosol Measurement», Van Nostrand Reinhold, pp. 6-46, (1993)
16. Keskinen J. et al. «Estimation of Effective Density of Diesel Particles», *J. Aerosol Sci.*, Vol. 29, Suppl. 1, S1007-S1008 (1998)
17. Moisio M. «Real Time Size Distribution Measurement of Combustion Aerosols» PhD thesis, Tampere University of Technology, Tampere (FIN), pp. 64-74.

CONTACT

Dr. Martin Mohr
EMPA
(Swiss Federal Laboratories for Materials Research and Testing)
Laboratory I.C. Engines/Furnaces
8600 Duebendorf, Switzerland,
Überlandstrasse 129
e-mail: martin.mohr@empa.ch

Definitions, Acronyms, Abbreviations

ACEA	Association of European Automobile Manufacturers
CPC	Condensation Particle Counter
CVS	Constant Volume Sampler
DF	Dilution factor
DI	Direct injection
DMA	Differential Mobility Analyser
d_p	Particle diameter
ECE	Economic Commission for Europe
EDC	European Driving Cycle
Ej. cold	Ejector with cold dilution air
Ej. hot	Ejector with hot dilution air
ELPI	Electrical Low Pressure Impactor
EMPA	Eidgenössische Materialprüfungs- und Forschungsanstalt (Swiss Federal Laboratories for Materials Testing and Research)
IDI	Indirect injection
NA	Natural aspired engine
NEDC2000	New European Driving Cycle 2000
nm	Nanometres = $1 \cdot 10^{-9}$ metres
NO _x	gaseous pollutant comprises NO and NO ₂
NSD	Number size distribution
PM	Particulate matter
ppm	Parts per million
Residue	Non soluble fraction
SI	Spark ignition
SINOF	Soluble inorganic fraction
SM	Single Mode Test
SMPS	Scanning Mobility Particle Sizer
SOF	Soluble Organic Fraction
TD	Thermodesorber