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Penetration of Diesel Particle Filters evaluated by various Soot Analyzing Techniques

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Abstract - Various types of particle filters to reduce particulate emissions of diesel engines in underground working areas have been tested. The precipitation efficiency have been evaluated, measuring particle size distribution in the submicron range by a TSI SMPS-system, total particulate matter (PM) by gravimetric analysis, elemental carbon (EC) by coulometric analysis of filter samples, black carbon (BC) by aetholemeter and photoemission (PE) of the submicron particles by the photoelectric aerosol sensor.

All methods (except PM analysis) show precipitation ratios for soot particles of the order of 2 decades and more for the tested filters. However the total particulate mass (PM) as determined by gravimetric analysis is only reduced by typically 1 decade. This large difference is due to material which passes the particle filter at temperatures above 300 °C in gasphase and condensates in the cooling down phase between particle filter and PM measuring filter, contributing the majority of the sampled PM mass. Soot particles from diesel engines with particle filters can therefore not be determined by gravimetric PM analysis.

As a result, legal PM emission measurement behind particle filters do not correlate with legal immission measurement in working areas of Germany and Switzerland, where the carbon concentration of soot particles with sizes below 5 μm is measured.

High concentrations of particles with sizes below 40 nm emitted from most particle filters at exhaust gas temperatures above typically 460 °C are identified as condensates by using a hydrocarbon vapor trap, a necessary tool to distinguish volatile droplets from non-volatile soot particles.

Additives in the diesel fuel are used to regenerate the tested particle filters. Their influence in the diesel combustion is a decrease of soot emission by several 10% as well as the appearance of additional small nonvolatile particles in sizes below 40 nm. Size selective analysis with soot sensitive sensors and with ICP-MS analysis of filter samples identified them as oxydes of the additive metals, which are precipitated in the particle filters down to uncritical concentrations.

Comparison between the different particle measurement techniques reveal good correlation between coulometric EC-analysis, BC- and PE-measurement by aethalometer and photoelectric aerosol sensor. The high time resolution and sensitivity as well as the simple maintenace of the photoeelectric aerosol sensor measurement are very favorable for it's use as a diesel soot monitor for static and dynamic controls in immissions and emissions.

1 Introduction

The investigation in testing soot reduction systems and methods as well as soot analyzing techniques is part of the project SUVA-VERT (Verminderung der Emissionen von Realmaschinen im Tunnelbau). Mean partners of this project [1] started 1994 and ending 1997 are

- **Suva** (Schweizerische Unfall-Versicherungs-Anstalt) Luzern
- **TGB** (Tiefbau Berufs-Genossenschaft) Germany
- **AUVA** (Allgemeine Unfall-Versicherungs-Anstalt) Austria)
- **BUWAL** (Bundesamt fürUmwelt, Wald und Landschaft) Bern
- **Ingenieurschule Biel**
- **ETH-Zürich, Laboratorium für Festkörperphysik**

and project management is done by

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and project management is done by

- **A. Mayer, TTM Niederrohrdorf**

Objective of this project is the reduction of emissions from diesel engines in working areas, initialized by the NEAT alpine tunnel project. Conventional air ventilating methods will not be sufficient to keep the pollution of ambient air during the tunnel construction phase below the legal MAK values. Fig 1 demonstrates that most attention has to be paid to the particulate emissions from diesel engines of construction machines.

mg/Nm^3	CO	NO_X	SO2	Particles
diesel engine emissions	1000	3000	350	250
MAK for working areas	35	30	5	0.2
required dilution factor	28	100	70	1250

fig 1 Diesel engine emissions and limits
(typical values for engines, used in construction sites)

Considering a typical exhaust volume of diesel engines of 6 m^3/kWh a minimal dilution air volume of the order of 750'000 m^3/h is requiered for a 100 kW-diesel engine to keep the particulate pollution of ambient air in tunnels below the legal limits by dilution. Therefore only emission reducing techniques such as particle filters or improved diesel combustion concerning particulate emission will be suited to solve this problem.

In the VERT programme 7 (July to Dec. 1996) as part of the SUVA-VERT project the characteristics of a sinter metal filter were tested on the test bench of Engineering School Biel with a 105 kW turbo diesel engine LIEBHERR type 914 T, using different particle analyzing techniques.

The particulate emissions of the diesel engine and the precipitation in the particle filter were studied

- in the submicron particle size range 15 .... 600 nm
- according to legal gravimetric PM measurement and coulometric carbon analysis
- with additional soot analyzing methods
- with distinction between volatile and nonvolatile aerosols
- with standard and sulfur free fuel
- with Ce- and Fe additives in the fuel

The predominant diesel particulate emissions consist of soot particles with sizes below 1 μ. Their main composition is elemental carbon (EC) and organic carbon (OC) as hydrocarbons. These particles are inhaled and deposited in the respiratory tract where they induce instantantaneous health effects and represent a risk for lung cancer. Particle size distribution measurement with the TSI SMPS system [2] is therefore a very important tool to analyze the submicron fraction of the emitted particles.

Legal test of diesel engines is done by sampling the total particulate matter (PM) on a measuring filter at 52 oC whereas diesel emissions in the ambient air of working areas is legally characterized by it's carbon concentration. The German TRK values (Technische Richt-Konzentration) are 0.1 mg EC in open areas and 0.3 mg EC in underground plants, The Swiss MAK value (Maximale Arbeits-Konzentration) is: 0.2 mg total carbon (TC = EC + OC). Both measurements were applied in the tests and additionally to the legal coulometric carbon measurement according to VDI 2465 [3], later described online soot analyzing methods for field use were tested.

The measurements were done on diluted diesel exhaust from a dilution tunnel AVL Smart Sampler II, mod. 472 according to legal standards (CH: FAV2) at the following 4 different operation points of the diesel engine according to ISO standard 8178

1) 1400 rpm, full load (typ. 88 kW)
2) 1400 rpm, 50 % load (typ. 44 kW)
3) 2000 rpm (nominal speed), full load (typ. 108 kW)
4) 2000 rpm (nominal speed), 50 % load (typ. 54 kW)

2 Measurements and results

Measurements with standard fuel

Fig 2 shows the size distribution measurement for the raw emissions, behind the particle filter and the calculated penetration of this filter which is below 1% over the entire sub-micron range. This excellent particle filter precipitation, measured on operation point 2) is seen at all additional operation points. The diesel engine is running with standard fuel.

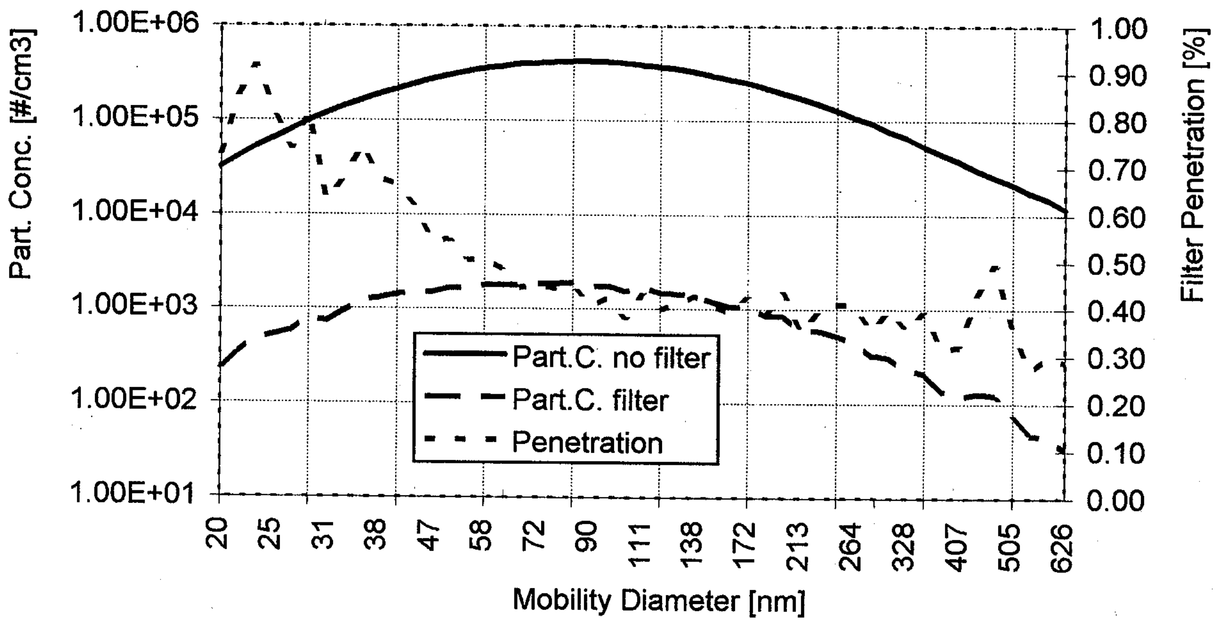


fig 2 Particle size distribution with and without particle filter for standard fuel

Comparison of gravimetric PM- and coulometric carbon analysis as well as the evaluation of the filter precipitation related to these quantities is shown in fig 3. The PM concentration in the raw emission is normalized to 100% and contains 88 % of total carbon (TC) or 76% of elemental carbon (EC).

This composition changes completely when a particle filter is used. The filter precipitaion deduced from EC-analysis is of the order of 2 magnitudes as also shown in fig 2, whereas PM-analysis leads to a much smaller value. The predominant composition of the PM filter sludge is material, which passes the particle filter at temperatures above 300 °C in the gas-phase and condenses in the cooling down phase between particle filter and PM measuring filter. Therefore this material cannot be soot.

This well established result means, that legal carbon measurement in ambient air of working areas and legal PM-analysis of diesel emissions when particle filter are used do not correlate.

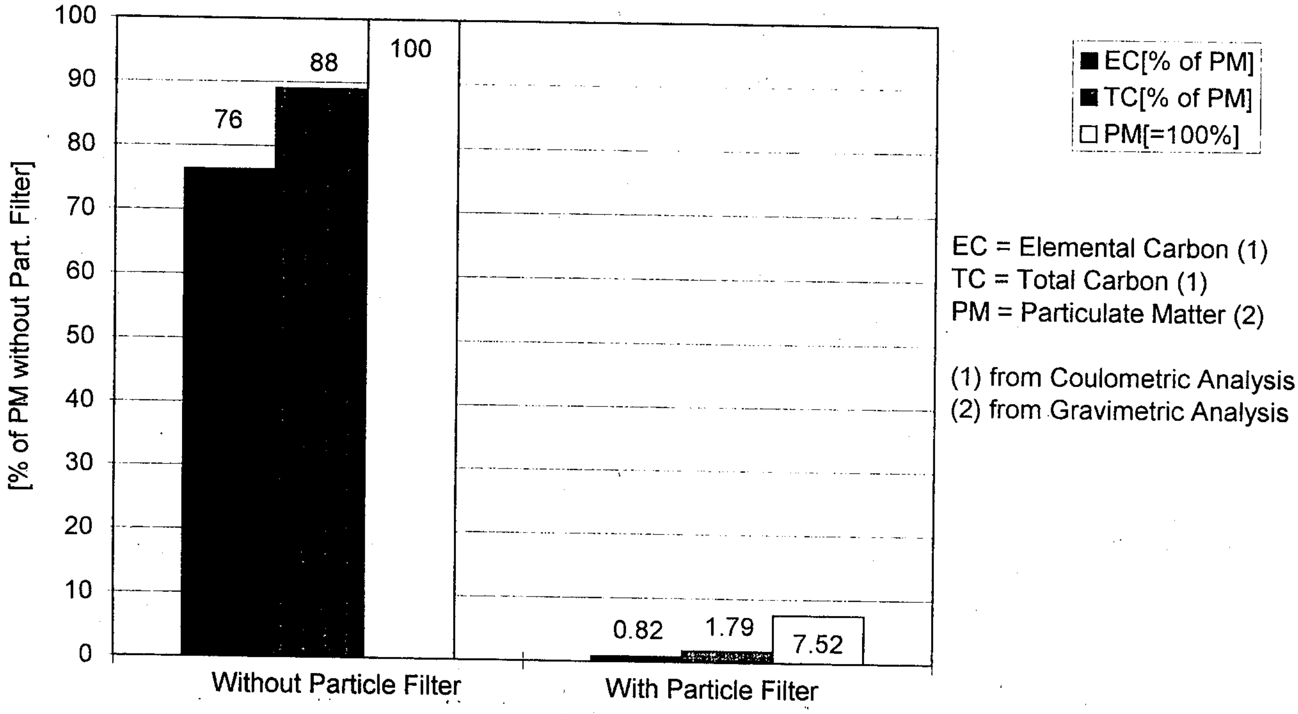


fig 3 Comparison of carbon concentration to gravimetric particulate matter (PM)

Measurements with additive in fuel

Most of the available particle filters are self regenerating (soot burn out) by additives, mixed in small concentration with the diesel fuel. Additives with Fe and Ce and their influence on the particulate emissions have been investigated. Fig 4 shows typical size distributions when the diesel engine is supplied with an additive in the fuel. Comparison with distributions from standard fuel supply reveals two significant influences:

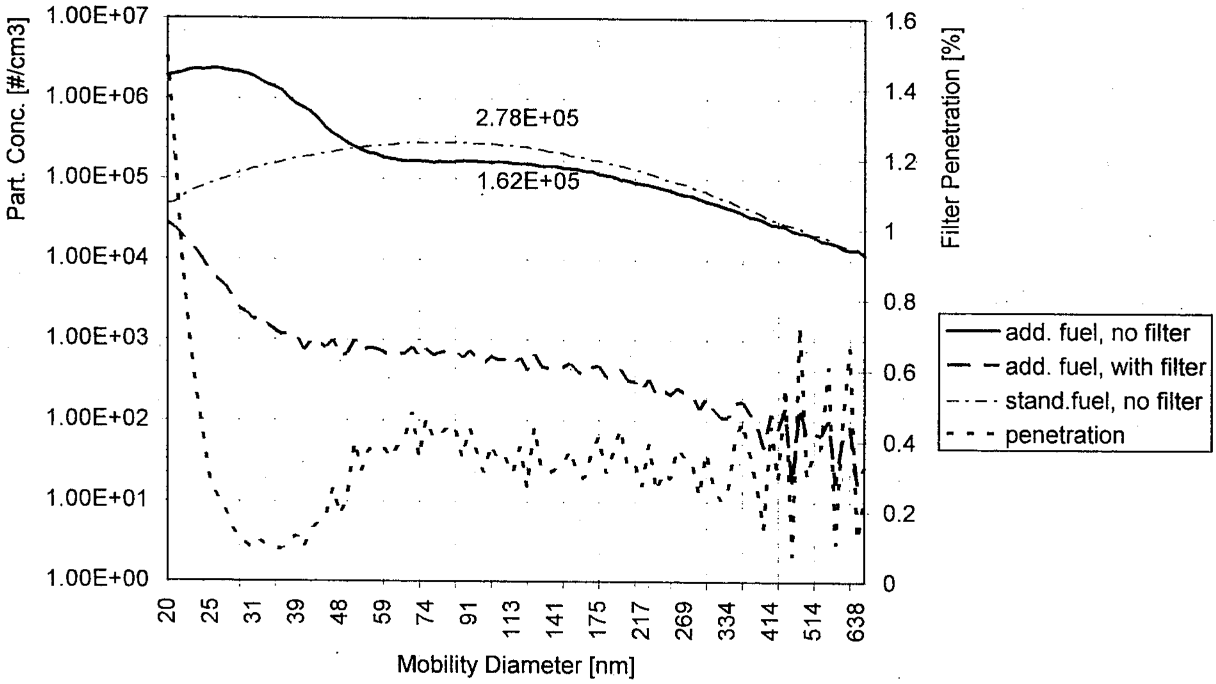


fig 4 Particle size distribution with and without particle filter for additive in fuel

- The soot particle concentration in the size range of 100nm is reduced by appr. 40%.
- New particles with sizes below 50 nm appear. Their size and concentration is varying depending on the operating condition of the engine and additive dosage.

The soot reduction is in agreements with studies of M. Kasper et. al. [4] and Jie Zhang et. al. [5] on laminar flames, where catalytic carbon oxydation by small Fe particles from ferrocene in the end phase of soot formation has been found.

Different investigations, e.g. in situ measurements and Inductive Coupled Plasma-Mass Spectroscopy (ICP-MS) filter-analysis on monodisperse particles as well as X-Ray Difraction (XRD) of ash from the particle filter prove that these additional particles are nonvolatile metal oxydes of the additive.

The oxyde particles are kept back in the particle filter with a satisfactory precipitation ratio of appr. 2 decades. Since these oxydes are not burned out like the soot, periodical cleaning of the filter is necessary.

Volatile particle formation in the filter

Depending on the operating condition of the engine the size distribution measurement reveals particles of sizes below 50 nm behind the filter in concentrations comparable to those of the raw emissions. This phenomenon appears reproducebly, when the temperature in the tested metal sinter filter exceeds appr. 460 °C. This temperature is achieved at operation point 3) with nominal speed, full load and maximum power.

The size distributions at this operation point are illustrated in fig 5 for the raw emissions and behind the particle filter

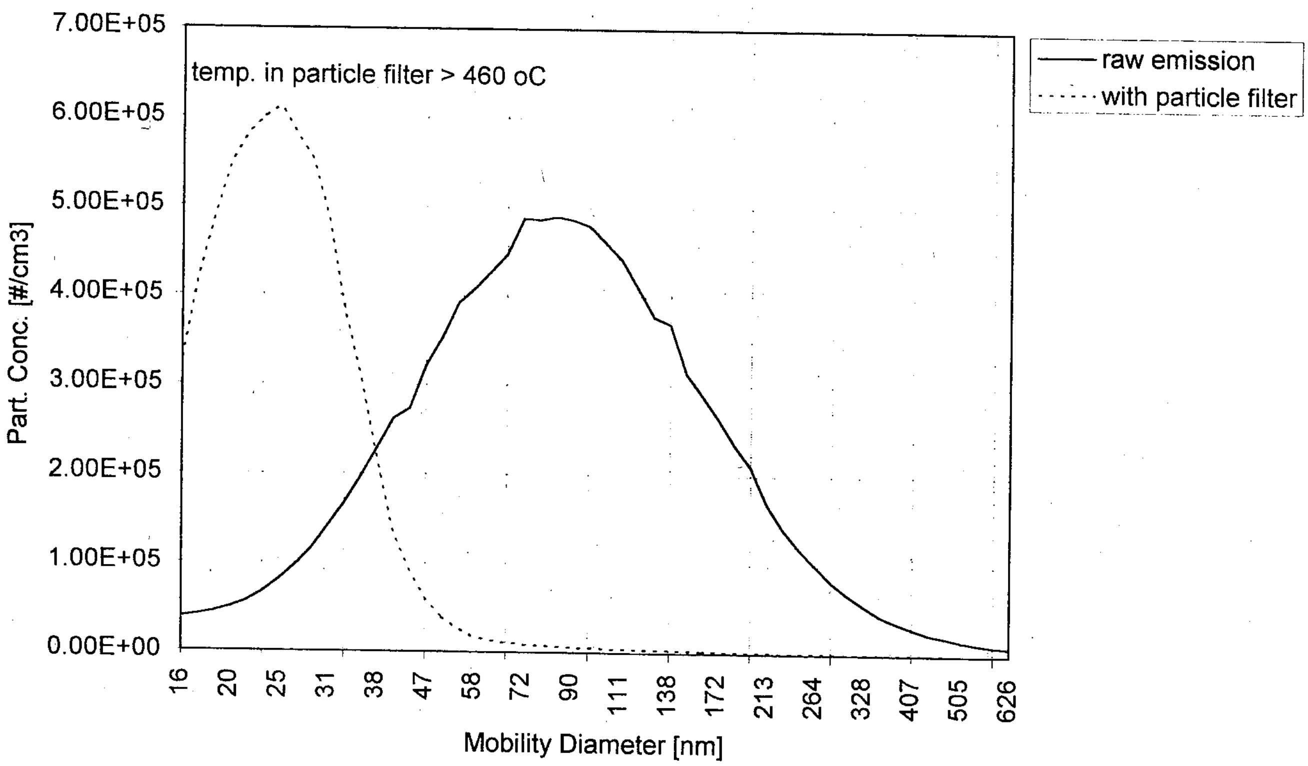


fig 5 Particle size distribution for volatile particle formation in the particle filter

A hydrocarbon vapor trap according to schematic diagram shown in fig 6 has been constructed and optimized to analyze the nature of these small particles. This vapor trap, introduced between dilution tunnel and measuring system allows to identify volatile particles with condensation temperatures between 50 and 300 °C. It removes the condensates, but lets the soot particles pass.

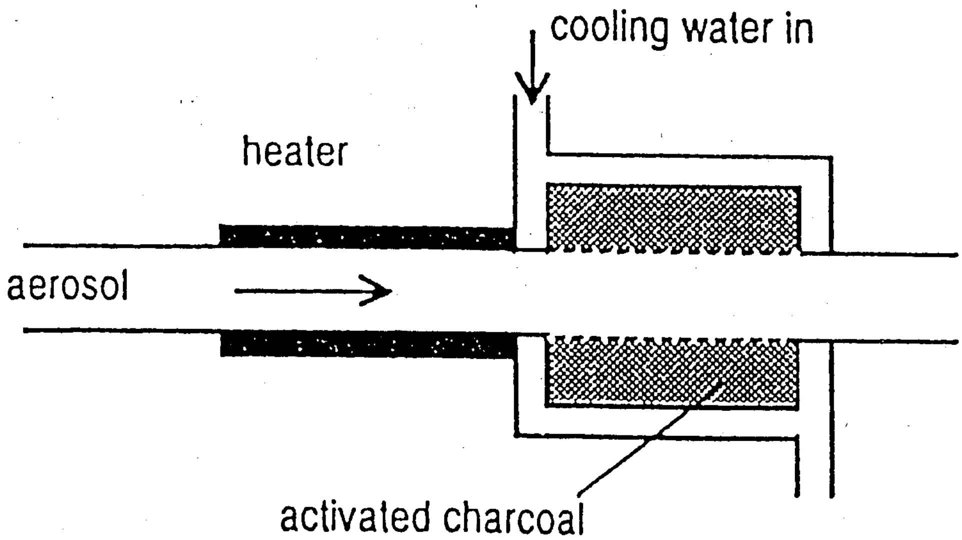
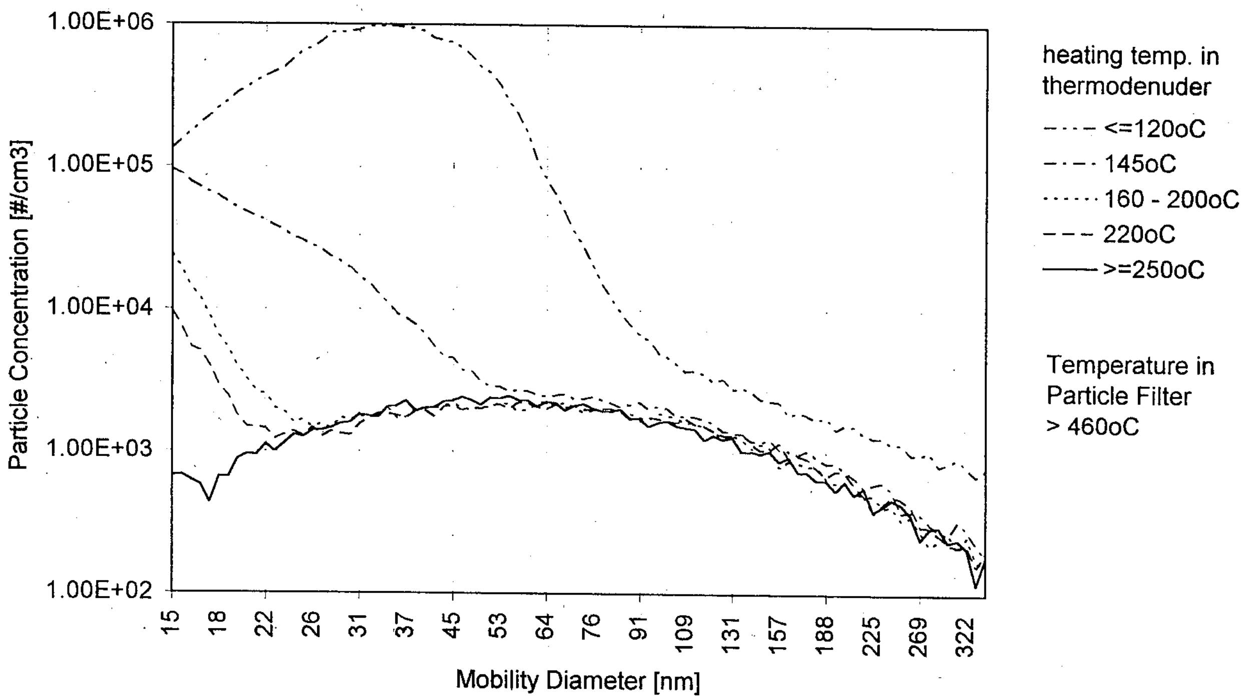


fig 6 Schematic diagram of hydrocarbon vapor trap

The result of the hydrocarbon vapor trap analysis is illustrated in fig 7. Size distributions have been measured on operation point 3) behind the particle filter on different heating temperatures in the vapor trap. Above 260 °C the distribution represents the nonvolatile soot particles which penetrate the filter with a precipitation ratio of appr. 2 decades. Cooling below 220 °C a first condensing substance appears and below 145 °C a second condensate with very high concentration is dominating the size distribution.

It is known from work on diesel catalysts that sulfates are formed in the exhaust in catalysts at temperatures above 460 °C [6]. This chemical reaction produces sulfur acid droplets in the exhaust cooling down phase. The volatile particles appearing below 145 °C are therefore probably sulfuric acid droplets whereas the material condensating below 220 °C might be a hydrocarbon.



Online soot analyzing techniques

SMPS size distribution measurement is a complex and laboratory orientated method which is unpracticable to be used in field applications. Gravimetric PM analysis doesn't give soot relevant information when particle filters are used, and both, PM and coulometric carbon filter analysis cannot record dynamic processes.

Two additional soot sensitive particle measuring instruments, the aethalometer and the photoelectric aerosol sensor were therefore investigated with respect to their characteristics for monitoring soot in the diluted diesel exhaust.

Aethalometer

Aethalometry [7] is a quasi-on-line measurement technique to determine the concentration of black carbon (BC). In the case of soot particles from diesel engines the BC signal correlates well with the concentration of elemental carbon (EC). The method is based on the fact that in filters covered with combustion aerosol, light is absorbed mainly by the elemental carbon. The aethalometer continuously measures the attenuation of a light beam going through a filter while the latter is being covered with aerosol particles.

At constant air flow, the rate of the increase of light absorption is measured at adjustable periodic time intervals. This allows continuous determination of the EC concentration at < 1 mg/m3 resolution at the time interval of 2 min.

Industrial versions of the aethalometer are sold by GIV ENVIRO, D 64747 Breuberg .

Photoelectric aerosol sensor

The photoelectric aerosol sensor was developed at ETH Zürich [8]. It monitors in real time the concentration of submicron particles from combustion processes.

The working principle of the monitor illustrated in block diagram fig 8 is based on the fact that combustion aerosols photo-emit electrons when they are irradiated with UV light (applied wavelength 185 nm and 222 nm). The charged particles are precipitated on a highly insulated particle filter and the charge current is measured. The photoemission signal in diesel exhaust correlates well with the concentration of elemental carbon.

Comparisons with chemical analysis of several types of combustion particles have and the photoelectric yield [9,10]. The sensors are therefore calibrated in particle bound PAH-concentration. This calibration is valid for urban air.

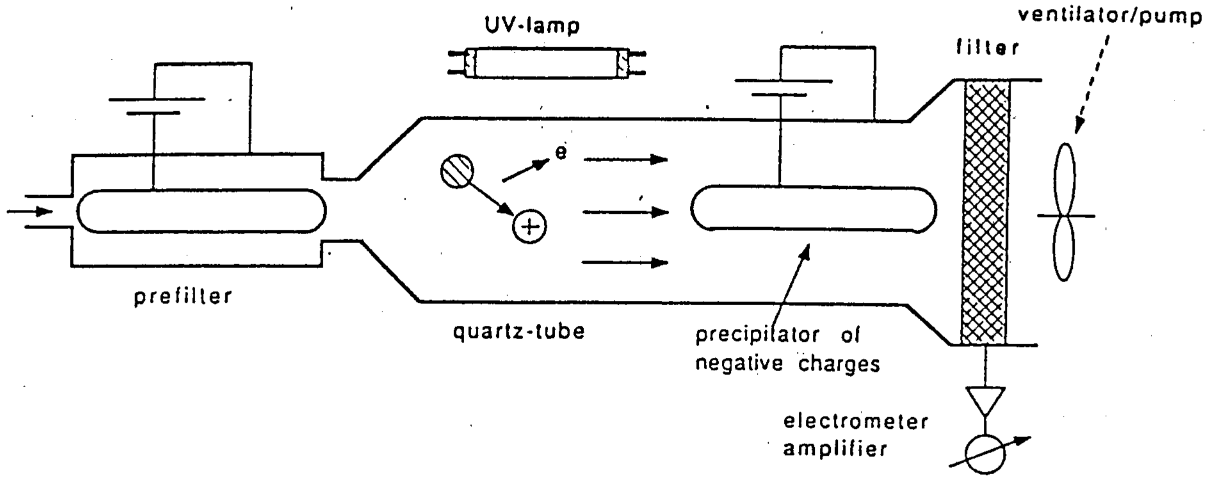


fig 8 Schematic diagram for photoelectric aerosol sensor

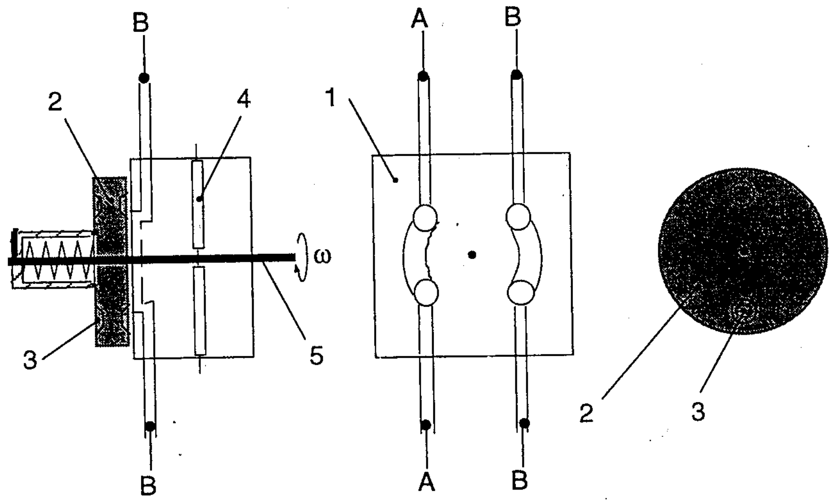
The photoelectric aerosol sensor is used as a monitor simple in use with high sensitivity and time resolution down to 1 s for soot particles in ambient air as well as in diesel exhaust.

Industrial versions of photoelectric aerosol sensors are sold by EcoChem Messtechnik GmbH,D 88682 Ueberlingen.

Adiustable dilution unit

Aethalometer and photoelectric aerosol sensor are dimensioned in sensitivity to such particle concentrations as occur in immission and workplace situations. In samples from the dilution tunnel the concentrations are typically by 1 to 2 decades higher, especially when no particle filter is used. For this situation a dynamic sample gas dilution stage was developed at the ETH [11] by means of a rotating disc with adjustable rotation frequency where small volumes of the undiluted aerosol are mixed with the dilution gas. The dilution ratio can be adjusted with accuracy over a range of more than two decades.

Dilution units as shown in schematic system setup fig 9 for ambient air and direct connection to undiluted exhaust in chimneys and exhaust pipes are sold by Matter Engineering AG,CH 5610 Wohlen



A aerosol channel — 1 body — 3 disk cavity — 5 rotation axis

B dilution fas channel — 2 rotating disk — 4 heating resistance

fig 9 schematic diagram for adjustable dilution unit

Comparison between different particle measurements techniques

The characteristics of aethalometer and photoelectric aerosol sensor have been investigated for two possible applications:

- Measurement of particle filter penetration by diesel soot particles.
- Monitoring of soot in diesel exhaust and correlation to coulometric carbon analysis.

Fig 10 shows the filter penetrations determined by all involved particle measuring methods, measured at the 4 operation points with standard fuel. For better illustration, the inverse of penetration is plotted on the vertical axis. The SMPS size distributions are analyzed in the 3 different representations as number, surface or volume concentration, where surface and volume are deduced from the analyzed mobility diameter.

To summarize, all methods except gravimetric PM analysis lead to penetrations of the same order of magnitude and therefore may be used to characterize particle filters with respect to the emiitted carbon in ambient air.

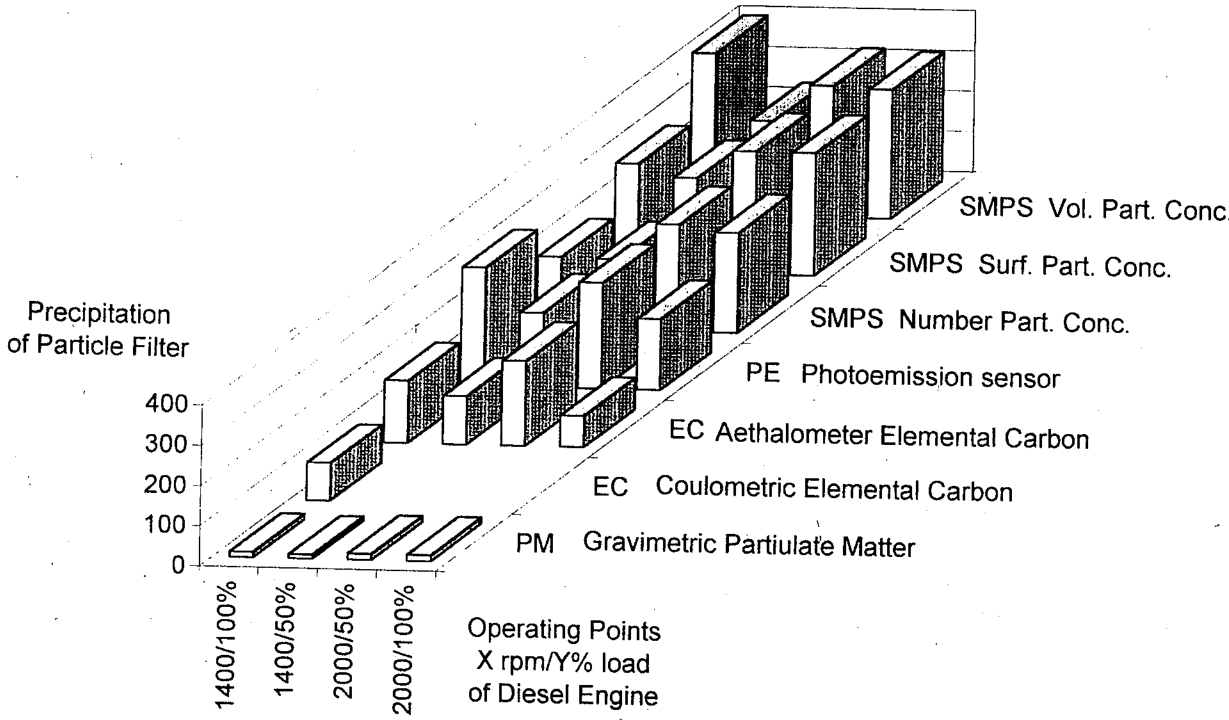


fig 10 Particle filter precipitation, evaluated by different particle measurement techniques

The correlation between aethalometer, photoelectric aerosol sensor and coulometric EC analysis are illustrated in fig 11 and fig 12. The photoemission signals are given in ng of particle bound PAH per m^3. This calibration is valid for urban air. In both figures a satisfactory good correlation between all three soot analyzing methods is evident.

Furthermore fig 11 illustrates the soot reducing effect of Ce and Fe additive. The soot reduction is not strongly affected when the additive dosing is reduced to 50% of nominal concentration.

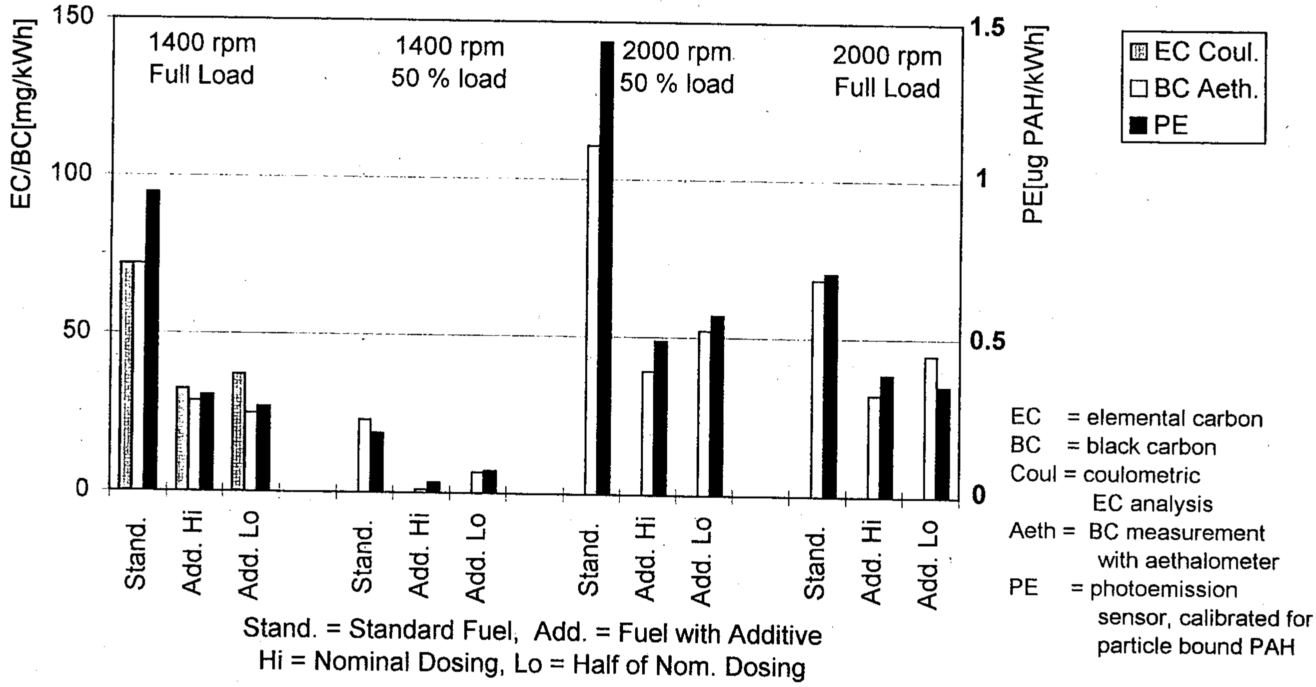


fig 11 Comparison of different soot analyzing methods on diesel soot

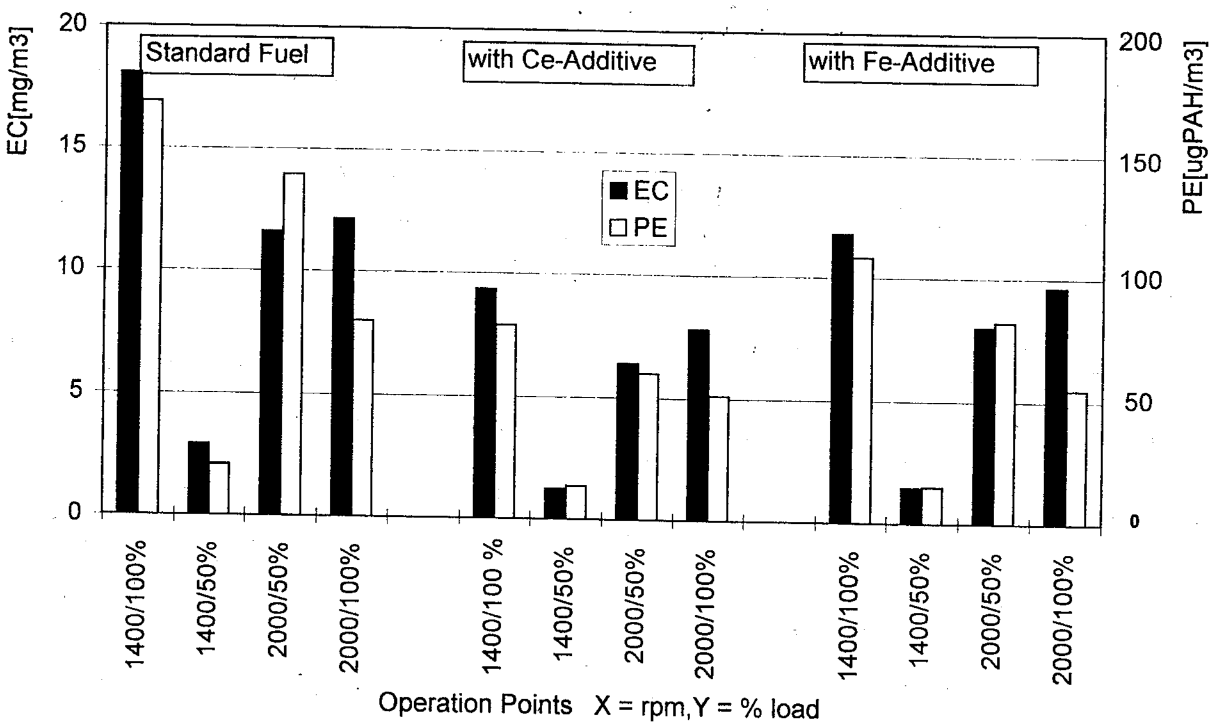


fig 12 Comparison of photoemission signal and coulometric EC-concentration on diesel soot

3 Conclusions

- The sinter metal particle filter as well as additional tested filters are able to reduce particulate emissions including the ultrafine particle fraction by 2 orders of magnitude and more. As a result of this positive evaluation, Suva, the Swiss authority for safety at the working place, will only permit diesel engines furnished with particle filters at underground construction sites.
- Different tested soot sensitive measuring techniques have been proven to correlate well with the EC concentration in diesel soot. These techniques are also suited to evaluate the penetration of nonvolatile respirable soot particles. The photoelectric aerosol sensor has been found to offer excellent qualifications for monitoring soot in field applications and for observing dynamic processes.
- Legal gravimetric PM analysis is not able to characterize the soot particles in diesel emissions when particle filters are used.
- Thermodenuding is a necessary tool to distinguish between condensates and non volatile soot in diesel emissions behind particle filters.

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