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PM10 in Switzerland

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VERT: Diesel Nano-Particulate Emissions: Properties and Reduction Strategies

PM10 in Switzerland

Abstract

In order to protect the population from excessive particle concentrations in inhaled air, ambient air quality standards for total suspended particulates (TSP) were laid down in the Swiss Ordinance on Air Pollution Control (OPAC) of 16 December 1985. However, recent scientific studies have shown that health may be impaired of particle levels below the current the ambient air quality standards. It was further established, that fine particles with a diameter of less than 10 µm (PM10) represent a good indicator for the health hazards resulting from of air pollution.

Fine particles can penetrate deep into the lungs and cause inflammatory reactions. High PM10 levels are associated with an increased incidence of complaints such as dyspnoea, persistent cough and phlegm, as well as respiratory diseases such as bronchitis. More frequent hospital admissions due to respiratory causes, a higher daily mortality and an increase in the long-term mortality rate are also observed. A report containing the latest findings on health effects of suspended particles has now been prepared by the Swiss Federal Commission of Air Hygiene (EKL) and recommendations concerning measurement techniques and ambient air quality standards for PM10 have been proposed.

(English abstract and summary of the report „Schwebestaub - Messung und gesundheitliche Bewertung", Schriftenreihe Nr. 270, Swiss Agency for the Environment, Forests and Landscape, Berne, 1996)

Summary

1. The acute harmful effects of dust as an air pollutant have been recognised for many years. Suspended dust particles from coal furnaces and industrial processes, along with a high concentration of sulphur dioxide, were known to be responsible for the increased mortality in post-war smog outbreaks in Europe and America. In the Swiss Ordinance on Air Pollution Control (OPAC) of 16 December 1985, which came into force on 1 March 1986, ambient air quality standards for total suspended particulates (TSP) were stipulated. The values were based on the current status of knowledge and experience at the time, and were set to 70 µg/m^3 as annual average and 150 µg/m^3 as the 95% of the 24-h-averages of a year. From recent scientific studies in Switzerland and elsewhere, it is now known that health may be impaired even if ambient air quality remains below these standards. It must therefore be concluded *either* that these ambient air quality standards are too high, *or* that the criterion adopted is inappropriate as a measure of the level of pollution. The scientific investigations carried out have now shown that both of these are the case.

2. The quantification of air pollution in towns, conglomerations and along busy transport routes in Switzerland has till now been based on NO_2 as typical indicator. However, recent epidemiological studies now show that particles of less than 10 µm (PM10 = particulate matter 10 µm) are more strongly correlated to human health effects than NO_2. The PM10, also referred to as thoracic fraction of the suspended particles, are those particles which, having passed the larynx, can finally penetrate in the lungs. At present, PM10 is the best available indicator for assessing health effects arising from air pollution. In addition to NO_2, it is therefore necessary to carry out systematic measurements of the PM10 fraction.

3. Included within PM10 are a variety of particles from primary sources such as combustion and industrial processes, and airborne road dust containing particles from brakes, tyres and road surface. A further constituent of PM10 are the aerosols formed in secondary reactions. Aerosols with the greatest relevance to human health are those arising from combustion processes in vehicles, furnaces and heating systems, as well as in industrial processes. Secondary aerosols i.e. nitrates, sulphates and ammonium, are formed from nitrogen dioxide, sulphur dioxide and ammonia, and arise from vehicles, furnaces, industry and agriculture. Combustion aerosols and secondary aerosols both belong to the group of very fine particles of size up to 2.5 µm (PM2.5). In addition to the PM2.5 particles, the PM10 fraction also includes airborne dust and particles from mechanical abrasion.

4. The measured PM10 value is strongly dependent on the measurement procedure. For this reason, measurement techniques for routine determination of PM10 in the inhaled air have been further developed and standardized over the

past few years. Switzerland was a member of the working groups (CEN, EU) concerned with harmonising PM10 measurement methods at European level. For purposes of comparison, several series of measurements are being carried out within Europe. These will enable international comparisons to be made. The technological infrastructure for PM10 measurements is presently available in Switzerland. In fact, by replacing the TSP sampling device by an approved PM10 device, any routine measurement instrument may be converted to PM10. In measuring PM10 and monitoring ambient air quality values, it will be necessary in cooperation with the Cercl'Air for the Swiss Federal Office of Environment, Forest and Landscape (BUWAL) and the Swiss Federal Materials Testing Institute (EMPA) to prepare recommendations for the measurement of PM10 for distribution to the cantonal and local authorities.

5. Complete sets of TSP measurements dating from 1981 onwards are available for seven sites of the National Air Pollutiant Monitoring Network (NABEL). The same measurement method was used at all sites. From 1987 onwards (in Lugano from 1990 onwards), a reduction of annual TSP concentration was observed. The annual ambient air quality standard of 70 $\mu g/m^3$ has not been exceeded at any NABEL site since 1993. In 1993, PM10 measurements were made for the first time in Switzerland under the National Research Programme (NFP 26) projects SAPALDIA and SCARPOL. The highest annual values recorded in 1993 were 33 $\mu g/m^3$ in Lugano and 30 $\mu g/m^3$ in Geneva and Basle. In 1995, PM10 was also measured at three NABEL sites. The ratio of PM10 to TSP varied from 0.57 to 0.81 depending on site location and time of year. From 1997 onwards, it is planned to monitor PM10 at all NABEL sites. TSP measurements will continue to be recorded only at selected sites.

6. There is a variety of health effects due to PM10. The fine particles can penetrate the bronchial tube, the bronchioles and the alveoli, impairing the lung's cleansing function and provoking inflammation. The precise biological mechanisms underlying the symptoms observed in the epidemiological studies are not yet fully understood. At high PM10 ambient air quality levels, the occurrence of dyspnoea, persistent cough and phlegm, as well as infections, aches and pains and diseases of the respiratory tract are more prevalent. Furthermore, existing diseases are worsened, lung function is reduced, and emergency room consultations and hospital admissions triggered by respiratory problems are more frequent. Also, the daily mortality and long-term mortality increase.

7. The studies show a linear, dose-response relationship between PM10 level and different short and long-term effects on human health. There was no evidence of the existence of a threshold value below which no effects were detectable. Recent Swiss studies within the NFP 26 have verified that these dose-response relationships are also applicable at pollution levels occuring in Switzerland. Thus for an increase in annual average PM10 concentration of 10 $\mu g/m^3$, pulmonary

function in Swiss adults was reduced on average by more than 3 %, and attacks of dyspnoea were 25 % more prevalent. For the same increase in pollution, 26 % more children suffered from respiratory infections, and 54 % more from persistent cough. Although the biological mechanisms are still not fully understood, the weight of scientific evidence is such that the existence of a causal relationship between air pollution and different health effects can hardly continue to be doubted.

8. In setting a ambient air quality standards for PM10, not only the variety of health effects (even at low concentrations, some of them, e.g. mortality, are irreversible), but also the existence of a linear dose-response relationship with no detectable threshold, must be taken into account. The Federal Law relating to the Protection of the Environment stipulates that effects on sensitive groups of persons are also to be considered. Included in this category are, e.g.: increase in mortality among the elderly and the sick, worsening of symptoms and reduction in the general quality of life among asthmatics and bronchitics, more frequent hospital admissions of older persons, increased use of medicaments, and more frequent respiratory complaints, diseases and persistent cough among children.

9. Based on the health effects for PM10 and NO_2 observed in Switzerland, a long-term ambient air quality standard for PM10 in the range of 15-20 $\mu g/m^3$ (annual average) would appear to be appropriate. The Swiss SAPALDIA and SCARPOL studies show that for an annual average PM10 concentration of 20 $\mu g/m^3$ an average 37 % of schoolchildren suffer from influenza and/or bronchitis, and 32 % from recurrent cough (i.e. more than four times per year). At the same concentration, 6% of adult non-smokers (i.e. those who never smoke) suffer from persistent cough or from phlegm discharge, and 7 % from dyspnoea. For purposes of comparison: at an annual average NO_2 concentration of 30 $\mu g/m^3$ (the ambient air quality standard in the Ordinance on Air Pollution Control), 38 % of schoolchildren suffer from influenza and/or bronchitis, and 35 % from persistent cough; among adult non-smokers, the results are the same as above - i.e. 6 % suffer from persistent cough or phlegm discharge and 7 % from dysnoea. Owing to the stronger correlation between PM10 and the health effects mentioned above in comparison to NO_2, and taking into account further effects observed world-wide including mortality, limiting criteria for PM10 should be chosen at least as strictly as for NO_2.

10. Deleterious effects on health occur likewise for short-term increases in PM10 concentration. A short-term ambient air quality standard must therefore be set for PM10 too. Owing to the acute effects of PM10, a short-term (24 h) ambient air quality standard in the order of 40 - 50 $\mu g/m^3$ would appear to be appropriate. In Switzerland, the available studies show that for a PM10 concentration of 10 $\mu g/m^3$ (daily average), a daily average mortality rate of 22.5 and 13 hospital admissions per million inhabitants through respiratory causes must be

expected. At a daily average of 50 µg/m^3, one additional death and one additional hospital admission occur. The relationship between the short-term and the long-term ambient air quality standard is of the same order for PM10 as for NO_2 (the proposed values being 40-50 µg/m^3 and 15-20 µg/m^3 for PM10, as opposed to 80 µg/m^3 and 30 µg/m^3 for NO_2).

11. Owing to the human health effects of suspended particles, and based on Articles 13 and 14 of the Federal Law relating to the Protection of the Environment, the Federal Commission of Air Hygiene (EKL) recommends to delete the existing TSP standards in the Ordinance on Air Pollution Control and to replace them by the following PM10 ambient air quality standards:

Annual average:	**20 µg/m^3**	
24-h-average:	**50 µg/m^3**	(may be exceeded once only per year)

12. Sustainability for air pollution also means, that the ambient air quality standards as laid down in the Ordinance on Air Pollution Control, which are based on clear-cut cause-and-effect relationships, are not exceeded. The Swiss guidelines on clean air policy emphasise effective and long-term measures to counteract excessive air pollution. NO_2 and ozone remain key indicators of excessive and chronic air pollution. The PM10 category represents a further important indicator of the extent of air pollution and its effects on human health. In addition to those already in force for NO_2 and ozone, effective measures must now be taken to control excessive immissions of PM10. These should include on the one hand technical measures to reduce particle emissions in the transport sector (particularly diesel engines), in industry and trade, in the combustion, and in the so-called "off road" sector (building, agriculture, aviation), as well as economic instruments (e.g. introduction of taxes on VOC and CO_2, and a mileage and emission dependent tax on heavy duty vehicles).

Concern about Diesel Particle

Emission during Tunnel construction

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VERT-Project

Suva, AUVA, TBG, BUWAL + Industrial Partners

Start 1993
Engine Test 93-97
Field-Test 95-97

Conclusion: Traps, filtering submicron Particles are available, technically feasible and cost effective.

Traps will be required for tunnel constructions sites in Germany, Switzerland and Austria.

↓

Enlarged application CH Off-Road

VERT: Diesel Nano-Particulate Emissions: Properties and Reduction Strategies

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1. ABSTRACT

Increasing concern, about the health risk due to solid aerosols from engine combustion, has provoked more stringent imission limits, for soot particles in the range of pulmonary intrusion, at critical work-places (e.g. tunnel sites, see Table 1). Within the scope of the joint European project VERT, these emissions were characterized and their effective curtailment through exhaust gas after-treatment investigated. Diesel engines, irrespective of design and operating point, emit solid particulates in the range of 100 nm, at concentrations above 10 million particulates per cm^3. Engine tests showed that a drastic curtailment of pulmonary intruding particulates seems not feasible by further development of the engine combustion, nor by reformulation of fuels, nor by deployment of oxidation catalytic converters. Particulate traps, however, can curtail the total solid particulate count, in the fine particulate range 15-500 nm, by more than two orders of magnitude. The effect can be reinforced through fuel additives, such as those promoting regeneration in particulate traps. A field test during 18 months (2000h) proved that several particulate trap systems meet this requirement. Thus the technical feasibility is basically established - the deployment of such particulate trap systems can therefore be demanded under critical exposures. Germany has already mandated the deployment of particulate traps in closed or partly closed working areas.

For the study of pulmonary intruding particulates from Diesel engines and the evaluation of the particulate traps systems, the usual gravimetric measurement of the particulate filtrate must be abandoned or at least enhanced. This is necessary as gravimetry is non-specific with respect to the chemical composition and the aerosol properties (such as size and surface) and, hence, delivers no toxically relevant information. The counted particulate concentration appears to be the significantly more specific and sensitive criterion. Industrially suitable and field deployable procedures should now be developed based on the dependable laboratory methods.

2. INTRODUCTION

VERT is a European joint project targeted at reducing the exhaust gas emissions, of existing Diesel engines, using commercial methods, in order to fulfil the recently tightened imission limits at tunnel sites. The Occupational Health Agency Suva (Switzerland), AUVA (Austria) and TBG (Germany) initiated the project in 1993 together with the Swiss Federal Environmental Agency BUWAL. A large group of industrial partners (manufacturers of Diesel engines, exhaust gas after-treatment, fuels and lubricants, measurement technology) participated from the beginning in the conception and implementation of the project. AISB, ETH, EAM and EMPA and Suva performed the measurements in Switzerland under TTM project management. After a two-year test period on engine test rigs, the emission curtailment measures were confirmed during 18 months of field tests on typical earth moving machines. These investigations are now completed. Preliminary results have been reported in several publications [1, 2].

The project began with the Swiss off-road emissions inventory. The values for a typical 100kW construction site Diesel engine are shown in Table 1 and compared with the prevalent imission limits in Switzerland and Germany.

The limits for CO, NO, NO_2, SO_2 can be controlled with the usual dilution methods. Fulfilling the particulate limits, however, would require an enormous technical effort (calculated at more than 1 million m^3 air per engine hourly!). This would exceed any feasibility at tunnel sites [2]. Consequently, dilution alone is insufficient for controlling imissions and it is essential to restrict emissions at the source. Particulate emissions must be restricted by improving the combustion or exhaust gas after-treatment. The target is a 100-fold reduction.

mg/Nm³	CO	NO	NO_2	SO_2	PM
Emissions	1000	2700	300 [1)]	350	250 (TPM) [2)]
Imission limits	35	30	5	5	0.2 (TC) [3)] 0.1 (EC) [4)]
Dilution	> 28	> 90	> 60	> 70	>2000

Table 1: Emission/Imission of DI-Diesel 100 kW [3]

1) fraction NO/NO_2 estimated
2) thereof typically about 200 mg/Nm³ carbon particulates
3) Total carbon = elementary carbon (EC) + organic carbon (OC)
4) Elementary carbon as per TRGS 554 [4], status 1997

Particulates enter the lungs through respiration, the deposition probability of the aerosol in the respiratory system increases with decreasing size [5] and the pulmonary defense against solid particulates is weaker than against water soluble condensates [6]. Hence, right from the start of the project, the focus was on the characterization and curtailment of solid aerosols and their adsorbates in the size range < 500 nm.

3. DEFINITION OF PARTICULATE EMISSION

There is great diversity in the definitions of prevalent regulatory limits. It is doubtful whether they are mutually consistent, representative of the impact mechanism, and sufficiently sensitive evaluation criteria.

The following definitions are prevalent:

- Road traffic: total filterable particulate mass at <52°C disregarding the chemical composition and aerosol properties.
- Off-road: the existing and envisaged international regulations have adopted the definition for road traffic.
- Imission Switzerland (new 1997): total filterable particulate mass < 10 μm (aerodynamic diameter) (PM10).
- Imission USA: total filterable particulate mass < 2.5 μm (PM 2.5).
- Workplace imissions in Swiss tunnels: total carbon (elementary carbon + organic carbon) for samples extracted as per the Johannesburg convention (50% at 5 μm).
- Workplace imissions in German tunnels: elementary carbon, samples extracted as per the Johannesburg convention.

These definitions are obviously not uniform. They differ in sampling technique, the analysis, and also the impact evaluation of substances and aerosol dimensions. The prevailing worldwide definition of TPM in road traffic has little significance and can easily cause a misleading evaluation of the efficiency of the applied measures.

There are on-going discussions [7] whether the German "elementary carbon" definition, that accounts for re-traceability, is sufficiently representative of the toxic criteria. The size evaluation according to the Johannesburg convention is long accepted but inadequate for the properties of combustion aerosols.

The VERT project selected a definition oriented towards toxicological criteria and is measurable with high accuracy: here the term "particulates" comprises all "aerosol solids in the size range 15-500 nm".

Fig. 1 compares the emission contributions of these fine particulates according to size, mass and surface. Clearly, the particulate count concentration, in the typical combustion aerosols size range, is the most sensitive criterion.

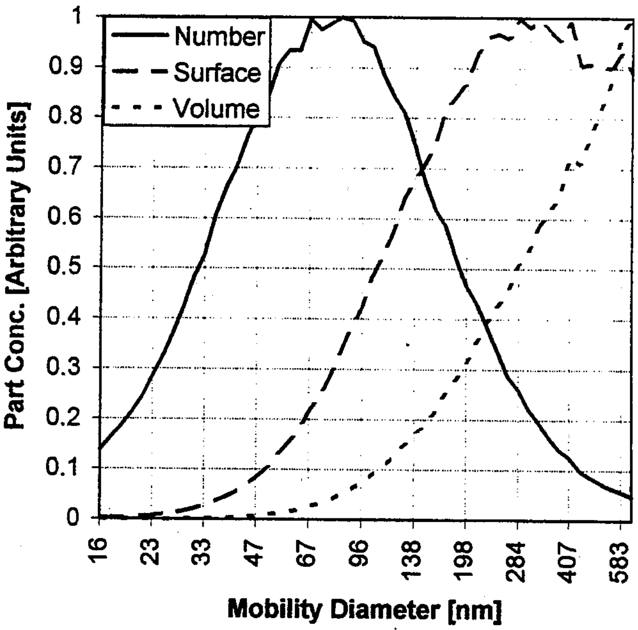


Fig 1: Size distribution of combustion aerosols according to counts, mass and surface (surface calculated from mobility diameter does not account for the morphology of the particulate agglomerates)

Previous emission and imission standards evaluate according to the mass. This is obviously inappropriate for the range of combustion aerosol distribution. The mass contribution of the many nano-particulates is negligible even at very high counts. The evaluation is then shifted to the "few" large particulates at the fringe of pulmonary intrusion. Therefore, efforts to reduce the nano-particulate cannot be clearly verified or evaluated using a mass criterion.

The evaluation according to particulate concentration count was therefore a priority in this VERT project.

4. ANALYSE METHODS

The exhaust gas for all tests were diluted as legislated (Switzerland: FAV II) in a partial flow tunnel (AVL Smart Sampler II, Model 472). Following methods were employed for measurement and characterization:

- Gravimetry according to the legally prescribed filter method;
  filter temperature < 52°C;
  filter material PALFLEX TX 40 HI 20 - WW;
  Particle mass as a rule about 1 mg;
  Weighing accuracy ± 1 µg
- Opacity measured as per Swiss regulations (device AVL 435)
- Bosch blackening method (device AVL 415)
- Particulate size distribution per particulate count: SMPS method: TSI 3934
- Particulate size distribution per mass: low pressure impactor Berner:
  impactor Andersen
- Aethalometry as a quasi-online measurement that correlates combustion aerosols well with elementary carbon (EC) concentration.
- Photoemission (device [8] developed by ETH/Matter and ECOCHEM), type LQ1, PAS 2000. It is a real time monitor for measuring the particulates and polycyclic aromatic hydrocarbons. The results correlate well with EC from Diesel engines.
- Coulometry to measure the elementary carbon and organic carbon as per VDI 2465.
- Separating the filter residues using the solution method into: elementary carbon, organic carbon, sulfate and water.
- Investigating the filter residue for metal content using x-ray fluorescence spectrometry, atom absorption spectrometry, plasma mass spectrometry and x-ray diffraction.
- PAH analysis using a combination of gas chromatography and mass spectrometry.
- Dioxins and Furanes using gas chromatography and mass spectrometry.

Most of these methods are internationally recognized and to some extent standardized. Only the photoemission is new and reveals interesting possibilities for real-time measurement.

Another novelty was aimed at distinguishing the solid particulates from the condensates. This task became urgent after the preliminary 1993 tests showed that cleaned gas, downstream of efficient particulate traps, nevertheless contained very high concentrations of spontaneous condensate. These strongly influenced the results and falsify the evaluations. Conditions prevailing at the relatively low dilution ratios favor the spontaneous condensation of hydrocarbons, water and sulfuric acid.

Fig. 2 shows the typical results of a 100 kW DI-Diesel engine at full load, run on low sulfur fuel (< 400 ppm).

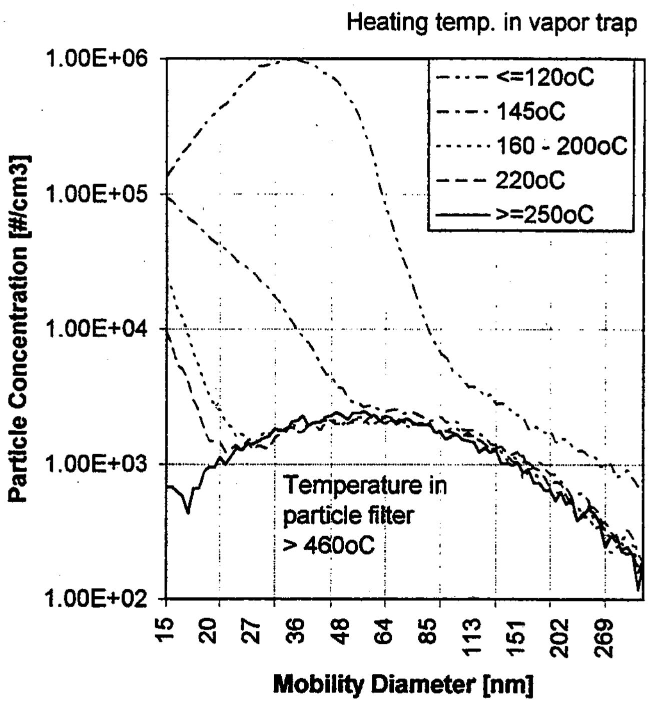


Fig. 2: Solid particulates and spontaneous condensate in diluted exhaust gas. Separation of solid and volatile substances using the active carbon trap as a function of gas temperature.

Without additional intervention, the SMPS method measures very high concentrations and a bimodal distribution at certain operational points close to full load (increased formation of SO_3 at exhaust gas temperatures above 450°C). Upon re-heating the exhaust gas after the dilution tunnel, some of these particulates disappear as a function of the re-heat temperature. The step-wise process indicates that these are products of sulfuric acids and hydrocarbons. Above 250°C the familiar distribution of solid combustion aerosols are mainly found at about 100 nm.

The analytical procedure using a heated active carbon trap was previously [1] described. This procedure to separate solid and volatile substances is regarded as generally essential for the nano-particulate analysis.

5. INFULENCE OF ENGINE CONSTRUCTION

The following engines were tested:

- Volkswagen: 1.6 ltr/4400 RPM / 44 kW / swirl chamber, turbocharging, no inter-cooling
- Audi: 2.5 ltr/4600 RPM / 88 kW / DI turbocharging, with inter-cooling
- Liebherr I: 914 TI: 6.11 ltr/2000 RPM / 105 kW / DI, turbocharging, no inter-cooling
- Liebherr II: 924 TI-E: 6.64 ltr/2000 RPM / 140 kW / DI, turbocharging with inter-cooling
- Caterpillar 3116: 6.6 ltr/2200 RPM / 127 kW / DI, turbocharging, no inter-cooling

Fig. 3 compares the particulate emissions (count concentration) of these five engines at an operating point close to full load.

All measurements were performed according to the SMPS method. Four different instruments were used, which permitted verification of the measurement accuracy. The SMPS method always delivered satisfactory results for concentration measurements and classification.

The general impression is that the combustion aerosols from Diesel engines are very uniform in the size range of 100 nm, and there is not much difference in their concentration of particulate count. Integrating the curve in the range 15-500 nm results in a total particulate count of 10^7 particulates/cm^3. There is evidence, that due to saturation the value of 10^8 p/cm^3 is generally not exceeded: the particulates agglomerate and the distribution slightly shifts to larger diameters.

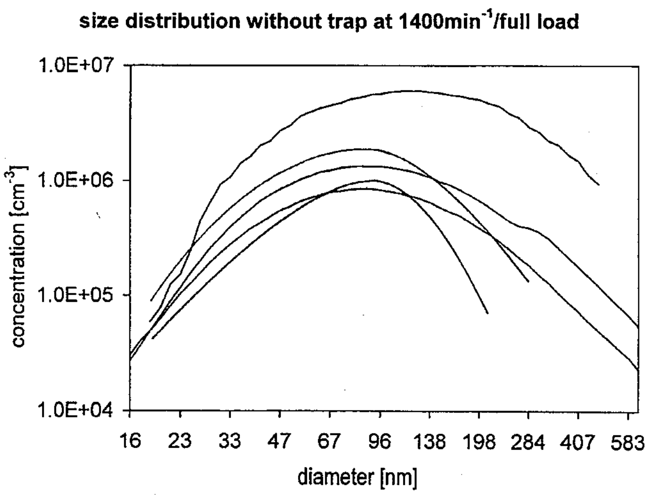


Fig. 3: Size distribution of particulate emission (concentration count) for 5 Diesel engines close to full load.

6. INFLUENCE OF LOAD AND RPM

Initially the tests were performed at a wide range of operating points. Further investigations were restricted to four important test points in the ISO 8178 C1 test cycle. These are full load at rated RPM and medium RPM, as also half load at those two speeds. These four points represent 50% of the weighting but at least 80% of the pollutant emissions. Further, they revealed important insights into the engine behavior in respect of practical deployment in construction site engines.

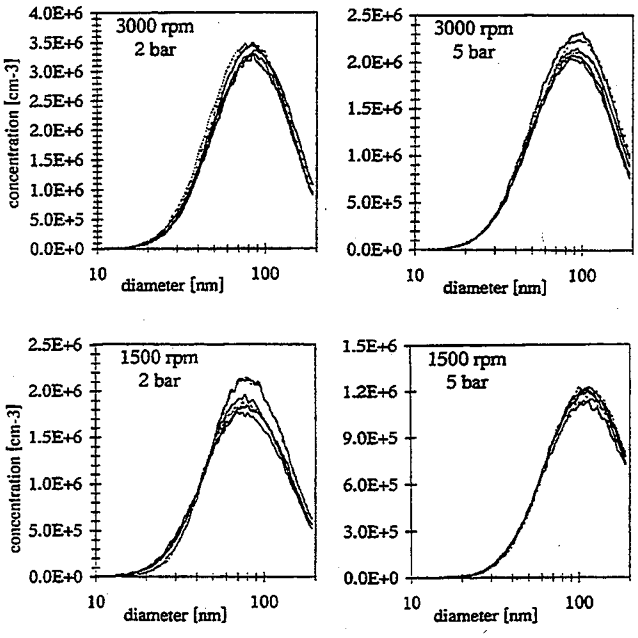


Fig. 4: Particulate size distribution of the VW engine at 4 load points

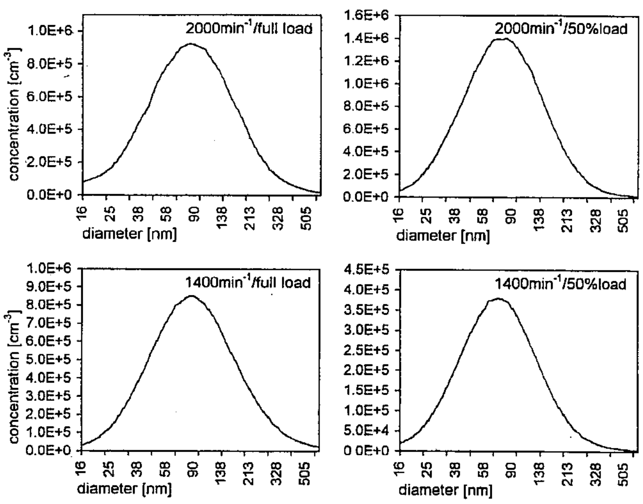


Fig. 5: Particulate size distribution of the Liebherr I engine at 4 load points.

The size distribution of the combustion aerosols from Diesel engines appear to be not strongly influenced design or load, neither regarding their size distribution nor their concentration count. Maybe substantially larger differences in combustion process parameters, e.g. temperature, oxygen content, mixture formation, dwell time, post-combustion conditions, etc. are needed to influence particulate size and concentration (e.g. in large marine engines or Starling engines).

The typical picture can thus be summarized as follows:

- Particulate diameter for Diesel engines: around 100 nm
- Concentration count for Diesel engines at the saturation limit: about 10^7 P/cm^3.

7. CURTAILING EMISSIONS THROUGH ENGINE MODIFICATIONS

Within the last decade, the engine development convincingly succeeded in reducing the particulate mass emission. Many engines today emit little more than 10% of the particulate mass usual 15-20 years ago. The successful engineering techniques are: high compression, air-intercooling, central nozzle position, increased number of nozzle perforations, very high injection pressures, suppressing the air swirl, and a shallow piston bowl. Together, these measures avoid combustion close to the walls and the mixture is prepared in the combustion air instead of at the surface. Thus, agglomeration is prevented, the black smoke disappears and with it the particulate mass reduced.

A low emission engine, certified 1996 in the USA, was employed to investigate the effects of these measures for nano-particulate emission reduction. This engine comprised all the constructional and process elements, described above for emission reduction.

The new engine has impressively low emissions compared to an engine from the same family developed 10 years ago. The nitrous oxides are halved and the fuel consumption substantially improved whilst the rated load was simultaneously boosted by 22%.

The nano-particulate distribution is here shown normalized as particulate count pro kWh. There is no detectable improvement. Indeed the low emission engine emits more fine particulates at all operating points; with a six-fold increase at one operating point.

Similar observations have been reported in other investigations [9]. The discussion of the Diesel engine combustion process (see section 13) generally concludes that curtailing particulates in the nano range, developments cannot be expected using these engineering. An increase is, however, theoretically plausible.

Hence the basic conclusion is that engine developments are unable to effectively suppress the formation and emission of nano particulates in high concentration counts.

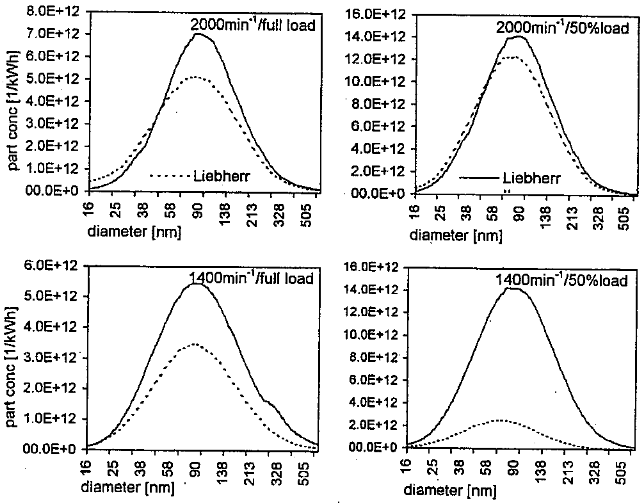


Fig. 6: Comparison of modern low emission engine vs. an older version of the same family at 4 load points.

Indeed it must be assumed that this is a fundamental observation for the combustion of hydrocarbons in engines.

8. CURTAILING EMISSIONS THROUGH FUEL OPTIMIZATION

The following two fuels were investigated to evaluate the long-term emission reduction potential of Diesel engines by reformulating the fuels:

The Swiss standard Diesel fuel was compared with a special fuel. It is a chemically pure paraffin fraction obtained from the DEA Fuels Ltd., Hamburg. This fuel contains neither Sulfur, nor bound Nitrogen, nor aromatics. It has such a high Cetane index that it must be viewed as an ideal Diesel fuel (as targeted by the current efforts for reformulating Diesel fuel, but that will probably never be attained using a mineral oil base). This fuel performed very well in the Diesel engine, resulting in an attractive fuel consumption but only 10% lower emissions. This is disappointing considering the high targets and expectations.

	CH-Diesel (SN EN 590 KO)	Special fuel (C14-20)
Density kg/m^3	0.815-0.845	0.780-0.790
Flame point °C	55	120
Boiling begins °C		240
Boiling ends 90% °C	360	360
Aromatic fraction %	< 30	< 0.1
Sulfur ppm	< 400	< 1.0
Cetane number	> 48	92 (index)
Values at rated load, Liebherr I:		
Fuel consumption g/kWh	221.2	210.7
at rated load kW	105.6	105.1
CO g/kWh	0.89	1.07
HC g/kWh	0.27	0.21
NOx g/kWh	13.3	11.56
PM g/kWh	0.115	0.103

Table 2: CH-Diesel and special fuel C14-20

The nano-particulate emissions were also measured in this fuel comparison. Fig. 7 illustrates the comparison at all four rating points.

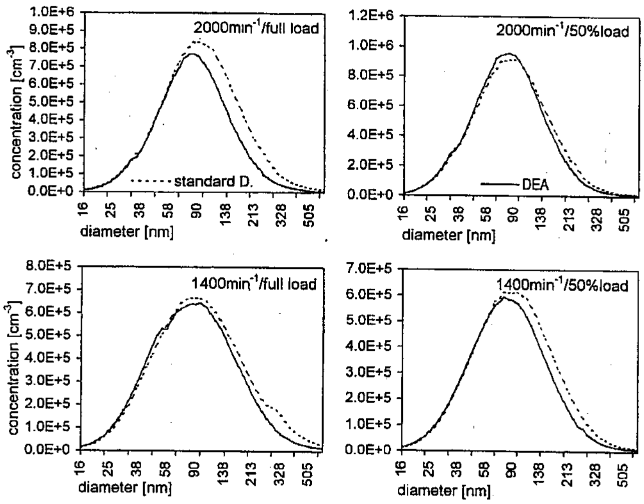


Fig. 7: Comparison of CH standard Diesel with special fuel (without sulfur and aromates)

Disappointingly, there is not the slightest amelioration in the emission of nano-particulate emissions. This is despite previous expectations for particulate curtailment, consequent to the very high Cetane number and the absence of Sulfur and aromatics.

This paradox can be explained with the new hypothesis of solid aerosols formation during combustion (see section 13).

One is tempted to conclude that no substantial curtailment of high nano-particulate concentrations can be achieved through fuel reformulation.

9. CURTAILING EMISSIONS USING OXIDATION CATALYTIC CONVERTERS

Oxidation catalytic converters are already widely deployed on Diesel engines. The converters are expected to curtail the automobile particulate emissions, particularly their soluble component.

Conditions are slightly different for utility engines than for automobile engines. The soluble fraction of the particulate mass is a smaller percentage. It is therefore questionable whether a reduction of solid particulate emissions is at all possible using oxidation catalytic converters.

The oxidation catalytic converter has various effects on the oxygen rich exhaust gas of the Diesel engine:

- desirable reactions
  $CO \rightarrow CO_2$
  $HC \rightarrow CO_2 + H_2O$
  Low CO and HC emissions of Diesel engines are attained, even without exhaust gas after-treatment, and are comparable to SI engines having 3-way catalytic converters. This is particularly evident in direct injection engines, usual in construction site engines.

- undesirable reactions
  $NO \rightarrow NO_2$
  $SO_2 \rightarrow SO_3$

  These reactions are judged disturbing, because NO_2 is much more toxic than NO (see Table 1), and SO_3 immediately forms sulfate particulate and sulfuric acid aerosols.

According to VERT experience, the gravimetric evaluation [1] does not show a reduction of particulate mass for utility engines. On the contrary, a significant increase in particulate mass is found.

Summarizing:

- The oxicat does not curtail the combustion particulates (soot).
- The oxicat produces sulfate particulates
- The oxicat has unfavorable gas phase reactions (raises the toxicity).
- The positive effects of the oxicat are irrelevant for the Diesel.

The influence of the oxidation catalytic converter on the nano particulate emissions is shown in Fig. 8.

Generally, the oxidation catalytic converter cannot curtail the actual solid combustion aerosols. This is not surprising, [10] because the catalytic combustion of soot proceeds much more slowly than the chemical conversion in the gas phase (the primary purpose of this catalytic converter). Further, the precious metals employed in conventional oxidation catalytic converters are unsuitable for burning soot.

The upper curve for full load clearly reproduces the formation of sulfuric acid aerosols (spontaneous condensate). These occur at very high temperatures, even without the catalytic converter. However, the catalytic converter intensifies the aerosol formation by accelerating the reaction $SO_2 \rightarrow SO_3$. This phenomenon is less noticeable at lower temperatures. The catalytic converter did not improve particulate emissions at any operating point.

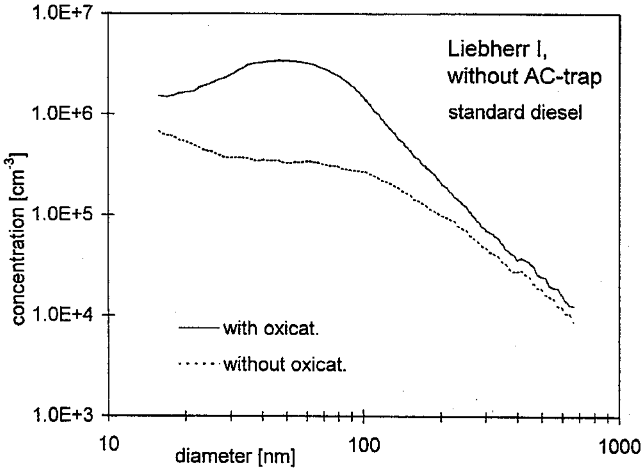


Fig. 8: Influence of oxicat on nano-particulate formation at full load, 2000 RPM

The inference is that oxidation catalytic converter shall not be deployed on utility Diesel engines, because the negative consequences far exceed the positive.

Further, there are indications [13], that solid particulates are formed in catalytic converters, based on the concept that the same reactions as in Diesel engine combustion also recur here at lower temperatures.

There is little hope that, engine modifications would make the particulates smaller and that the oxidation catalytic converter can burn them away without residues. As shown in [10], these reactions are so much slower that the catalysis of gaseous substances, that the intermediate retention in a trap cannot be avoided.

10. CURTAILING EMISSIONS USING PARTICULATE TRAPS

The properties of particulate traps in filtering nano particulates were previously [1, 11] compared. Many traps very efficiently arrest the larger particulates but fail in the nano range. Others are uniformly effective in their retention performance. The true deep bed filters are even more effective in the range of extremely fine particulates.

These observations were substantiated with the refined measurement technique of this project. Figures 9 to 11 illustrate the results from 5 traps considered typical and therefore representative of the latest technical level.

The results demonstrate the very impressive efficiency of many traps in retaining solid combustion aerosols within the entire size range. The filtration efficiency is 99% and more.

This is valid, according to present results, for new traps at all investigated operating points. How and whether the filter performance changes during operation is under investigation.

Occasionally, increased penetration is observed in overloaded or under-dimensioned surface filters. Deep bed filters, however, maintain their high filtration rates of finest particulates. The examination of trap characteristics, under various operating conditions, must however be continued. Trap damage, even leaks through microscopic perforations, probably cause a rapid increase in the nano particulate penetration.

11. CURTAILING EMISSIONS USING A FUEL ADDITIVE

Fuel additives are employed in so-called passive particulate trap systems. These additives have a catalytic effect and light-off all residual soot in the traps. This regeneration occurs at about 350°C (for the typical soot composition of utility engines). Three leading products are commercially available for test purposes:

- satacen/Pluto, additive: Iron
- Eolys/Rhône Poulenc, additive: Cerium
- Lubrizol, additive: Copper

The additives are metal organic compounds, mix well with the fuel and participate quasi-molecular in the combustion.

These fuel additives generally have a positive influence on the energy specific mass emissions, as shown in Table 3.

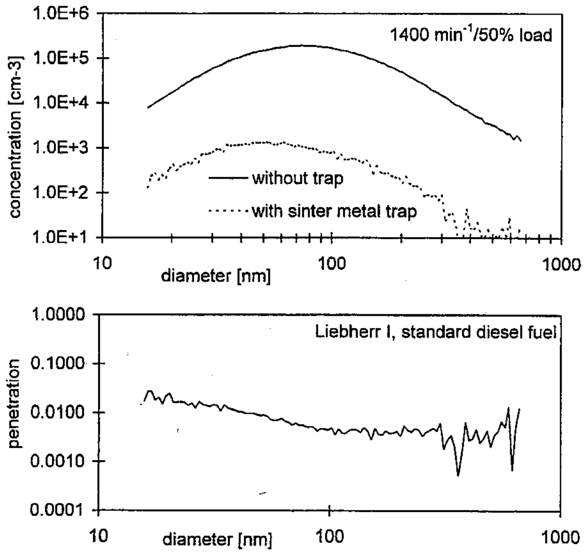


Fig. 9: Filtration characteristic of an sintered metal trap

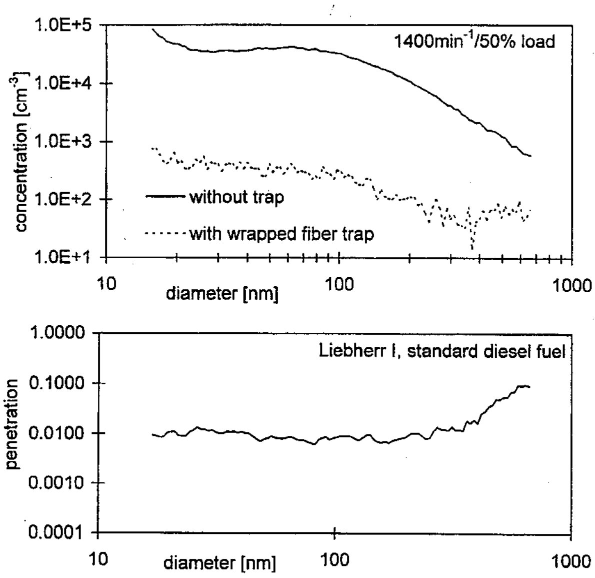


Fig. 10: Filtration characteristic of a wound fiber filter

%		HC	NOx	PM
Ce	no filter	125	110	87
Ce	with filter	90	92	65
Fe	no filter	120	107	90
Fe	with filter	90	92	50
Cu	no filter	132	110	87
Cu	with filter	112	95	50

Table 3: Emissions using fuel additives at full load/rated RPM on the Liebherr II engine (100% is fuel without additive).

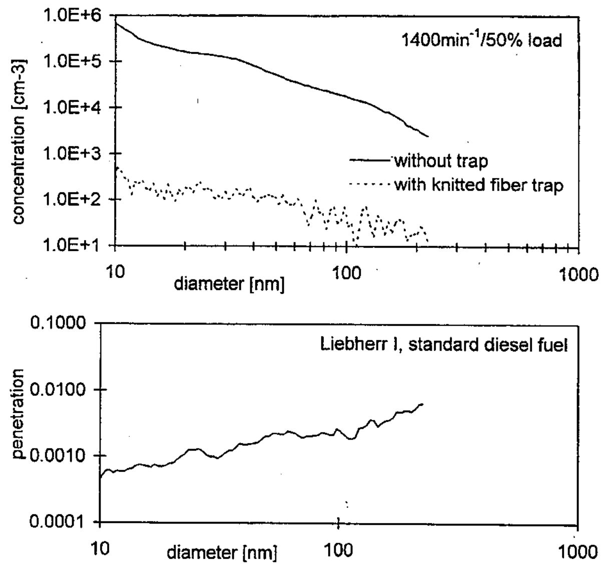


Fig. 11: Filtration characteristic of a knitted fiber trap

The additive substances oxidize during combustion. Their oxides are catalytically active because of the different oxidation stages, a typical property of these so-called transitionary metals. The additive oxides form tiny particulates (probably about 10 nm) that adhere to the soot particulates. They catalyze the carbon oxidation during the combustion and also after deposition in the trap.

The oxide particulates are expected to be mostly bound to the soot particulates. However, it cannot be excluded that free oxide particulates are present in the nano-range.

Examples of the particulate size distribution using such fuel additives is shown for satacen at a standard concentration of 18 mg Iron/kg fuel in Fig. 12 and for Eloys with a standard concentration of 50 mg Cer/kg fuel in Fig. 13.

These fuel additives curtail the soot emission both in the nano range and in the total gravimetric evaluation. This is noticeable both in the raw gas as also in the treated gas after the trap. Thus the efficiency of the system to alleviate particulate emission is improved in two ways.

However, the additives do indeed form metal oxide particulates that are much smaller than those of the carbon particulates. Depending on metal oxide concentration, the emissions in the finest size class are higher than without additives. This is extremely undesirable and basically not toxicologically permissible for many additives.

Hence, additives shall not be used without a trap. Further, when using particulate traps, a filtration characteristic must be chosen that is sufficiently efficient and durable in this lowest particulate size range.

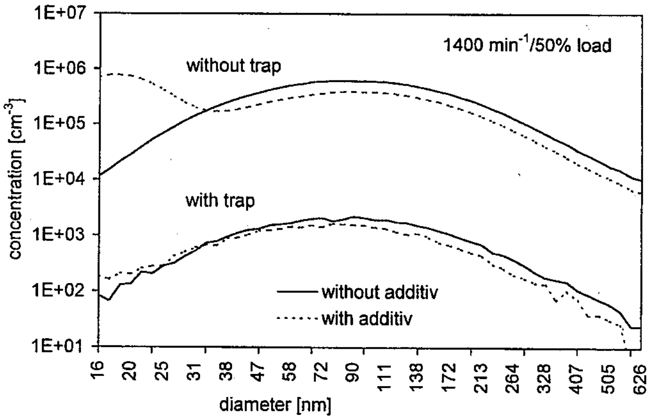


Fig. 12: Nano-particulate emissions using satacen/ Pluto, with/without filter.

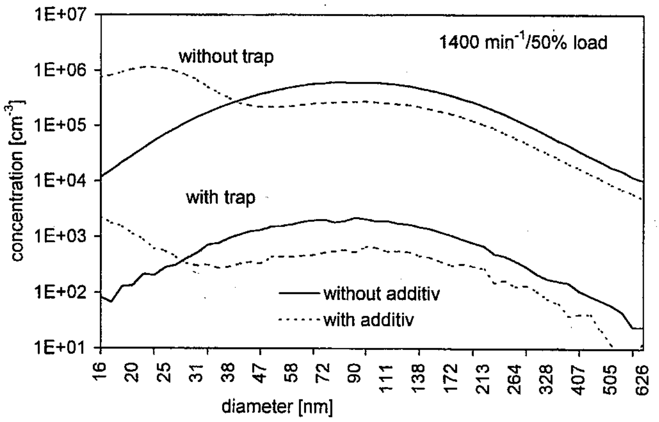
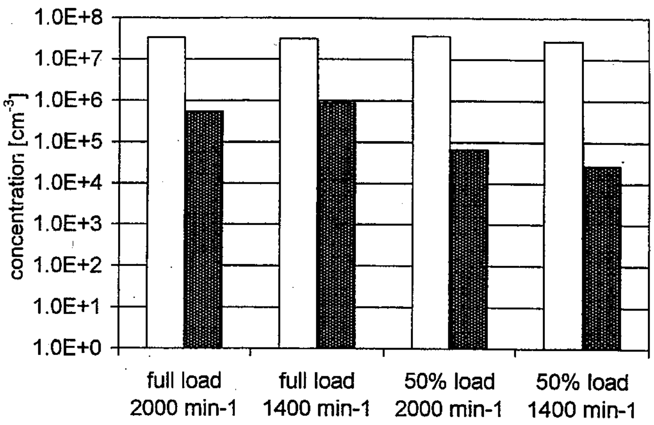


Fig. 13: Nano-particulate emissions using EOLYS / Rhône Poulenc, with/without filter.

Fig. 14 shows the integration of the particulates in the entire size range from 20-500 nm, for all four operating points and an increased additive concentration with 36 mg Iron per kg fuel. The baseline without particulate trap and without additive is compared to the combination of particulate trap and fuel additive.

The figure shows, too, that the use of additives to ensure passive regeneration also improves the trapping efficiency significantly. There is a curtailment of three orders of magnitude at the two low-load operating points. The heated active carbon trap was not operating at the two full-load points. Hence, the results were negatively influenced by spontaneous condensate. Nevertheless, here too, the total evaluation shows an improvement of two orders of magnitude.



□ without trap, standard Diesel fuel
■ with trap, satacen 36 ppm

Fig. 14: Integrated particulate concentrations in the size range 20 - 500 nm. Standard Diesel fuel compared to satacen additive fuel (36 ppm Fe).

12. TRAP EVALUATION USING DIFFERENT MEASUREMENT METHODS

According to the gravimetric criterion, the trap quality is defined by the ratio of the total filtered mass at < 52°C, before and after the trap. This comprises the solid mass of the actual combustion aerosols (soot). It also comprises the condensate mass of substances that pass the filter in the gaseous state (HC, SO_2, SO_3, H_2O), at the trap's operating temperature, but then condense on the measurement filter and are thus gravimetrically equated as soot.

$$\text{Penetration} = \frac{(M_{\text{Particulate}} + M_{\text{Condensate}})_{\text{after trap}}}{(M_{\text{Particulate}} + M_{\text{Condensate}})_{\text{before trap}}}$$

Filtration rate = 1 - Penetration

Even if the trap penetration of solid particulates was = 0, there nevertheless remains a finite gravimetric value because of the condensate content. According to Fig. 15, penetrations of 0.1, i.e. filtration rates of 90% are measured.

All other measurement methods in Fig. 15 show substantially better values, i.e. penetrations in the range 1 - 2% and thus filtration efficiency of 98 to 99%. Coulometry, which is generally considered to be a reference method, measures a filtration efficiency of 99%. Aethalometry, calibrated against EC, has a similar value. Both those methods mainly consider larger particles. Photoemission and the SMPS evaluation indicate even better values because they better detect the small and almost invisible lighter particulates. They show a filtration efficiency of up to 99.7% for the same trap.

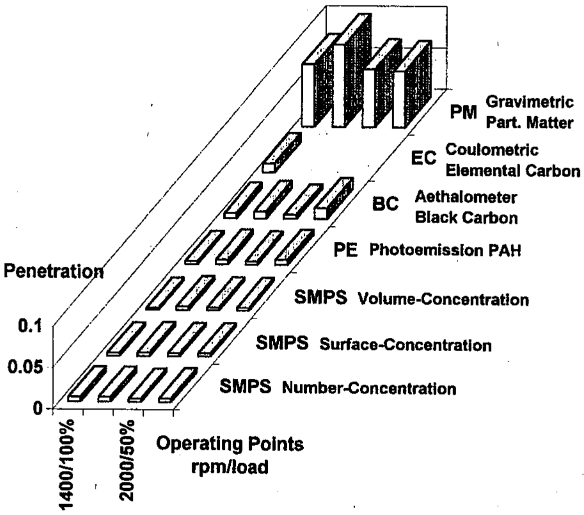


Fig. 15: Filter evaluation using different measurement methods.

Hence, the gravimetric evaluation of filtration is inappropriate, due to false assignment of the condensates, and is misleading for the trap development. If ever gravimetry is used, then a substance-specific analysis must be supplemented, e.g. using a two step coulometric procedure.

13. HYPOTHESIS ON THE ORIGIN OF COMBUSTION AEROSOLS

In contrast to the earlier hypothesis of coking droplet residues, or the acetylene theory, a new physical hypothesis is here postulated. This hypothesis is a result of the accompanying research activities at the ETH [12] and the EAM [13]. This postulates: the fuel injected in minute droplets, vaporizes rapidly at the high temperatures in the combustion space. The hydrocarbons that shall now react with the air Oxygen are essentially present disassociated, and the links between C and H are broken. Combustion occurs at the surface of such a cloud of Hydrogen and Carbon atoms. As hydrogen diffuses about 10 times faster than Carbon into this combustion zone, the cloud is rapidly devoid of Oxygen. Carbon reacts much slower, remains behind, and some of its atoms form carbon clusters via the free valences, particularly in the Oxygen deficit. These clusters subsequently agglomerate to primary particulates. Their structure is disordered, in any case not really graphitic, otherwise they would be more stable. Parallel to this process, new Hydrocarbons are formed from the primary substances C and H. These Hydrocarbons mainly have polycyclic structures that survive the after-burning process because of their very high chemical stability. The gaseous Hydrocarbons enter the exhaust gas and, upon cooling, condense onto the solid particulates. This process is promoted through oxygen deficit and extremely short combustion duration.

These processes can be well observed [12 and 13] in individual flames.

This hypothesis explains why particulates occur in similar size and number almost independent of the fuel composition. Compared to gasoline, Diesel fuel has only the disadvantage that it has less Hydrogen. The Diesel process would therefore be further disadvantaged, when insufficient mixture preparation and short combustion periods can more likely cause a local Oxygen deficit in the droplet range, compared to the fully homogenous mixing of gaseous reaction substances.

14. OPPORTUNITIES FOR AN INDUSTRIAL MEASUREMENT TECHNIQUE

The measurement procedures employed in these investigations, e.g. the SMPS procedure and the Coulometry are complex measurement processes. They are mainly suitable for laboratory conditions. They are unsuitable for wide scale industrial deployment, e.g. in workshops or in the field. On the other hand, the usual gravimetric method is questionable, because it is completely unspecific to the chemical composition of the particulates and their aerosol attributes. There is an urgent necessity to develop a new measurement method. The project investigations confirmed that photoemission is a very simple robust and cost effective method. It has a very good correlation to the referential methods of Coulometry and SMPS. Photoemission is a promising development.

Controlled cooling and dilution of the exhaust gases is a pre-requisite for all sampling. Conventional dilution tunnels are cumbersome, complex and problematic because of the danger of particulate aging. Here too, a new concept [8] describes the miniaturized quasi-digital dilution technique.

15. CONCLUSIONS

The evaluation of Diesel exhaust gas, on the basis of imission criteria, shows that the pulmonary intruding finest particulates (elementary soot) are very harmful pollutants. Pulmonary damage occurs because of their miniature dimension, very high active surface, chemical composition, and very high concentrations found in all engines and in all operating states. No improvements can be anticipated from further development in the engine combustion, reformulation of fuels and lubricants, and after-treatment through oxidation catalytic converters. Very effective are traps, particularly deep bed filters exposing high adhesive surfaces and able to retain the nano particulates with very high efficiencies.

The evaluation of the traps, as also the general pollution classification of the Diesel exhaust gas, must be done size-selective and substance-selective. The standard methods such as gravimetry are not suitable. Laboratory methods such as electrical mobility according to the SMPS method are reliable [11]. Also Aethalometry and Photoemission are promising. However, suitable procedures for industrial deployment are not yet available.

Within the VERT project several filter systems have been investigated that satisfy the stringent criteria and proved themselves in over 2000 hours of field deployment. These systems are partially in the prototype stage. Efforts must be increasingly focussed on developing these trap systems for large-scale deployment, in order to use them widely for the efficient filtration of nano particulates from engine exhaust gases.

16. ACKNOWLEDGMENT

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ACRONYMS

AISB	Abgasstelle der Ingenieurschule Biel (Exhaust gas lab/Polytechnic Biel)
AUVA	Österreichische Allgemeine Unfallversicherungsanstalt (Austrian Accident Insurance Agency)
BUWAL	Bundesamt für Umwelt Wald und Landschaft (Swiss Environmental Protection Agency)
EAM	Eidgenössische Amt für Messwesen (Swiss Federal Office of Metrology)
EC	Elementary carbon
OC	Organic carbon
TC	Total carbon = EC + OC (2 stage Coulometry)
EMPA	Eidgenössische Materialprüfungs- und Forschungsanstalt/Dübendorf (Swiss material testing agency)
ETH	Eidgenössische Technische Hochschule (Swiss Federal Technical University)
PSI	Paul Scherrer Institut (ETH)
SMPS	Scanning Mobility Particle Sizer
Suva	Schweizerische Unfall Versicherungs Anstalt (Swiss National Accident Insurance Organization)
TBG	Deutsche Tiefbauberufsgenossenschaft (German Association of Construction Professionals)
TRGS	Technical regulations for hazardous materials
TRK	Technical guidelines for concentration
TTM	Engineering Consultants, Niederrohrdorf Switzerland
VERT	Project to curtail the emissions from engines at tunnel sites