# Definition of Diesel Particulate

or Diesel-emitted Particles ?

**Actual legal Definition:**

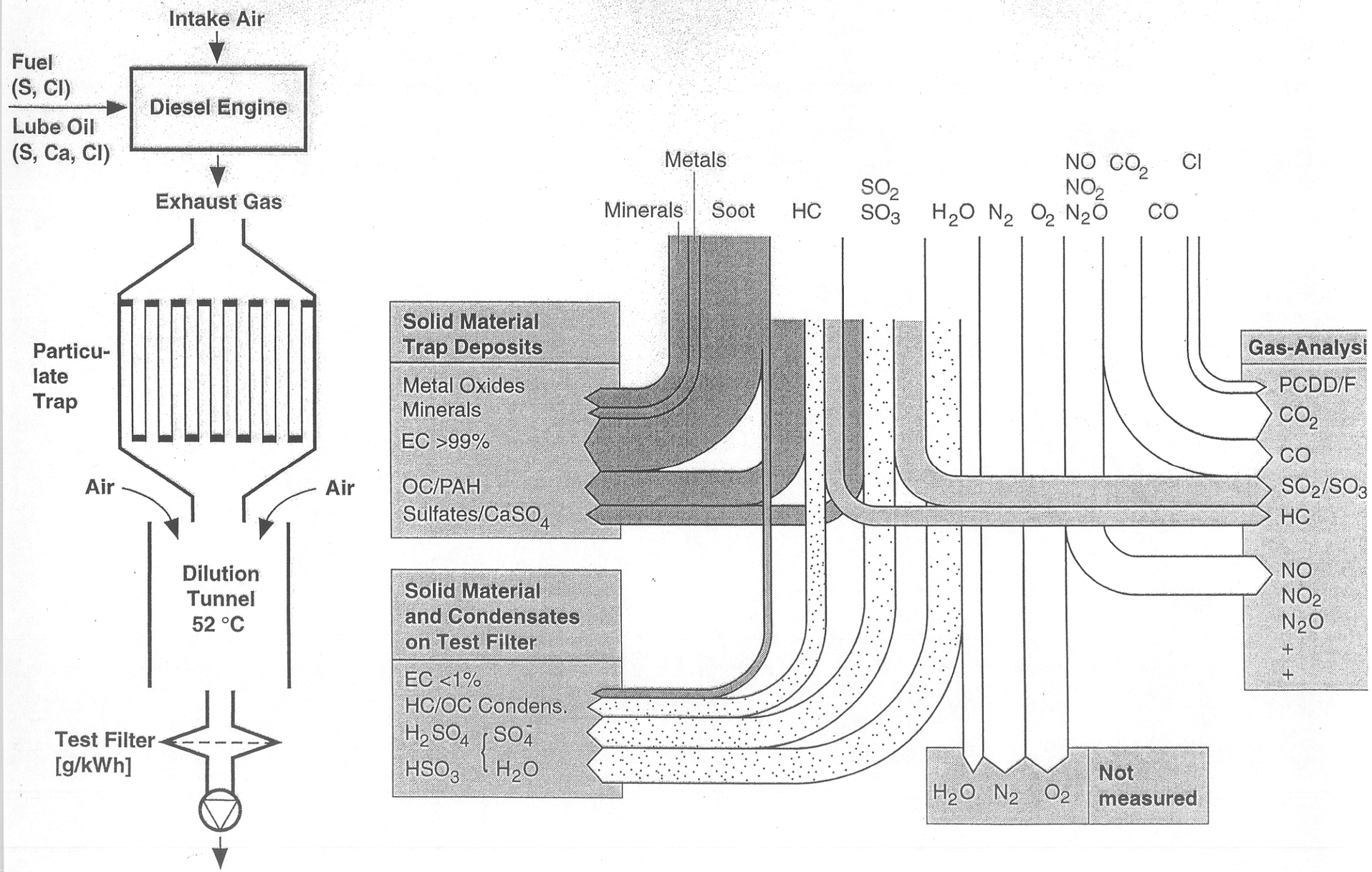
anything filtered from CVS-tunnel at temperatures < 52 °C
irrespective of size ( 1 P. of 1μm = 1000'000 P. of 10 nm)
irrespective of chemical substance (could as well be water)
irrespective of health effects ?)

**Swiss VERT-Definition:**

Solid Particles
and anything adsorbed to it
at tail-pipe conditions
in the size range 10-500 nm

# Flow Sheet «Engine/Trap» and Particulate Measurement

TTM / 20.2.1999



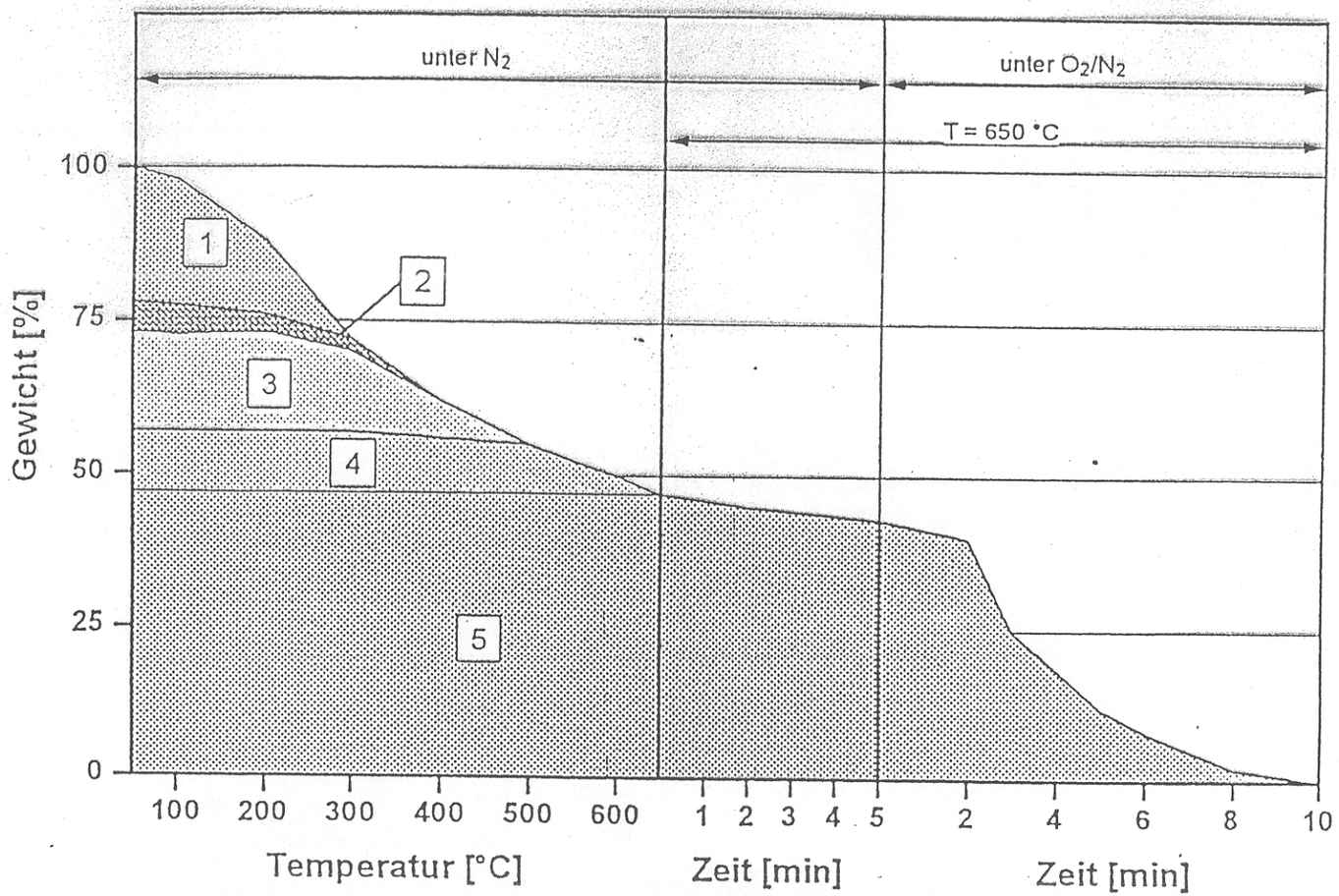
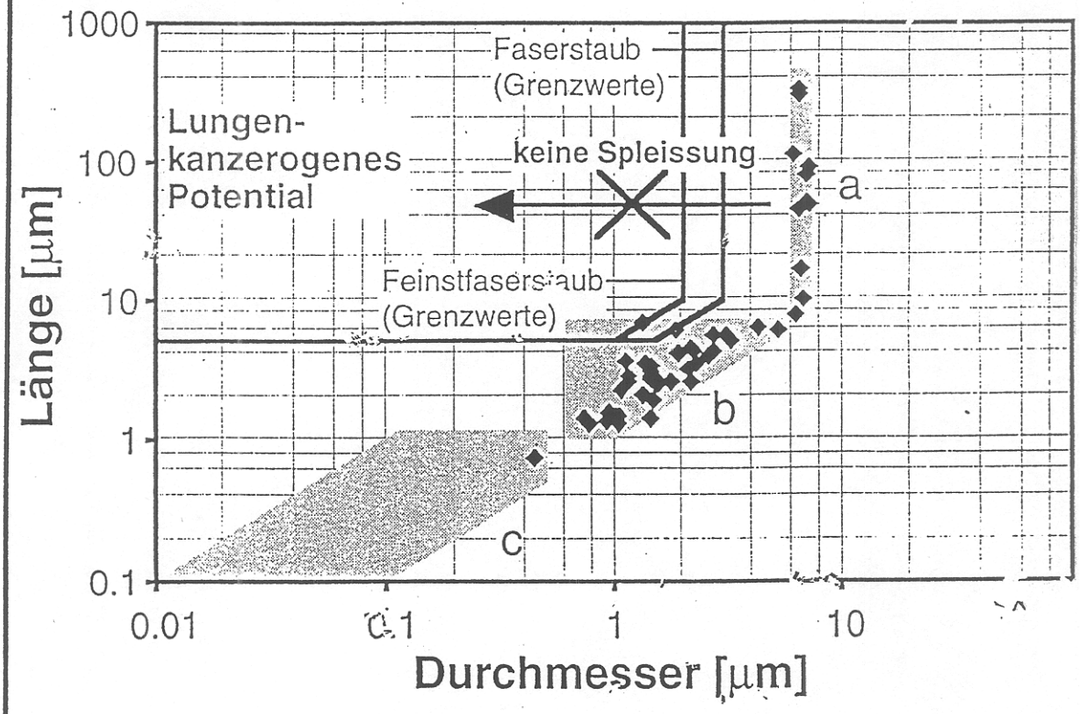
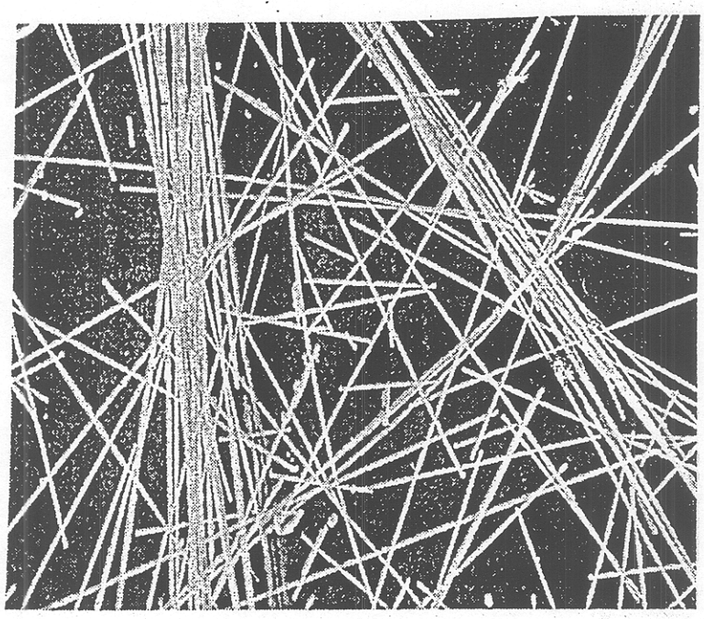



Bild 7.3-4: Typisches Thermogramm einer Partikelprobe:

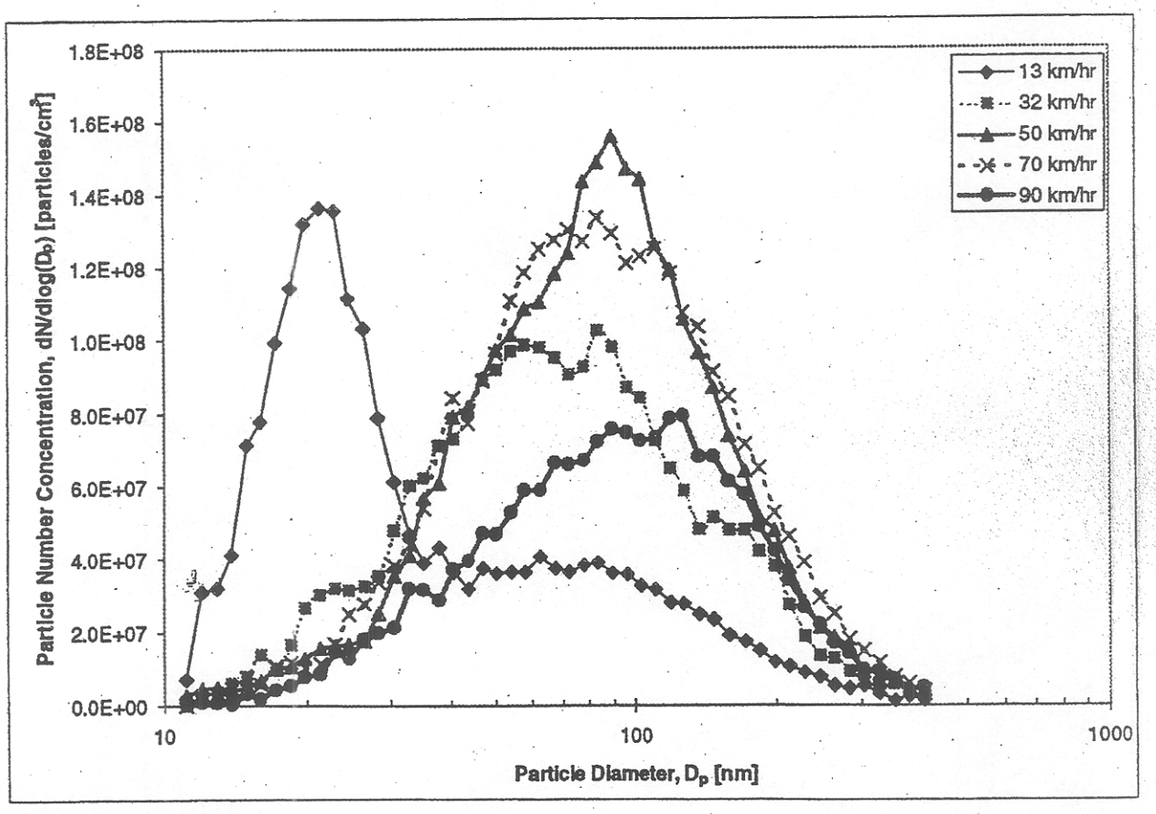
1: niedrig-siedende Kohlenwasserstoffe (Kraftstoff)
2: Sulfate und Wasser
3: höher-siedende Kohlenwasserstoffe (Öl)
4: Desorption, Dehydrogenation, Rußstrukturänderungen
5: Ruß



| | | |
|---|---|---|
| BUCK TTM | **Gesundheitsrisiko bei Einsatz von Mikrofasern** | HdT Essen 17./18.9.1996 |

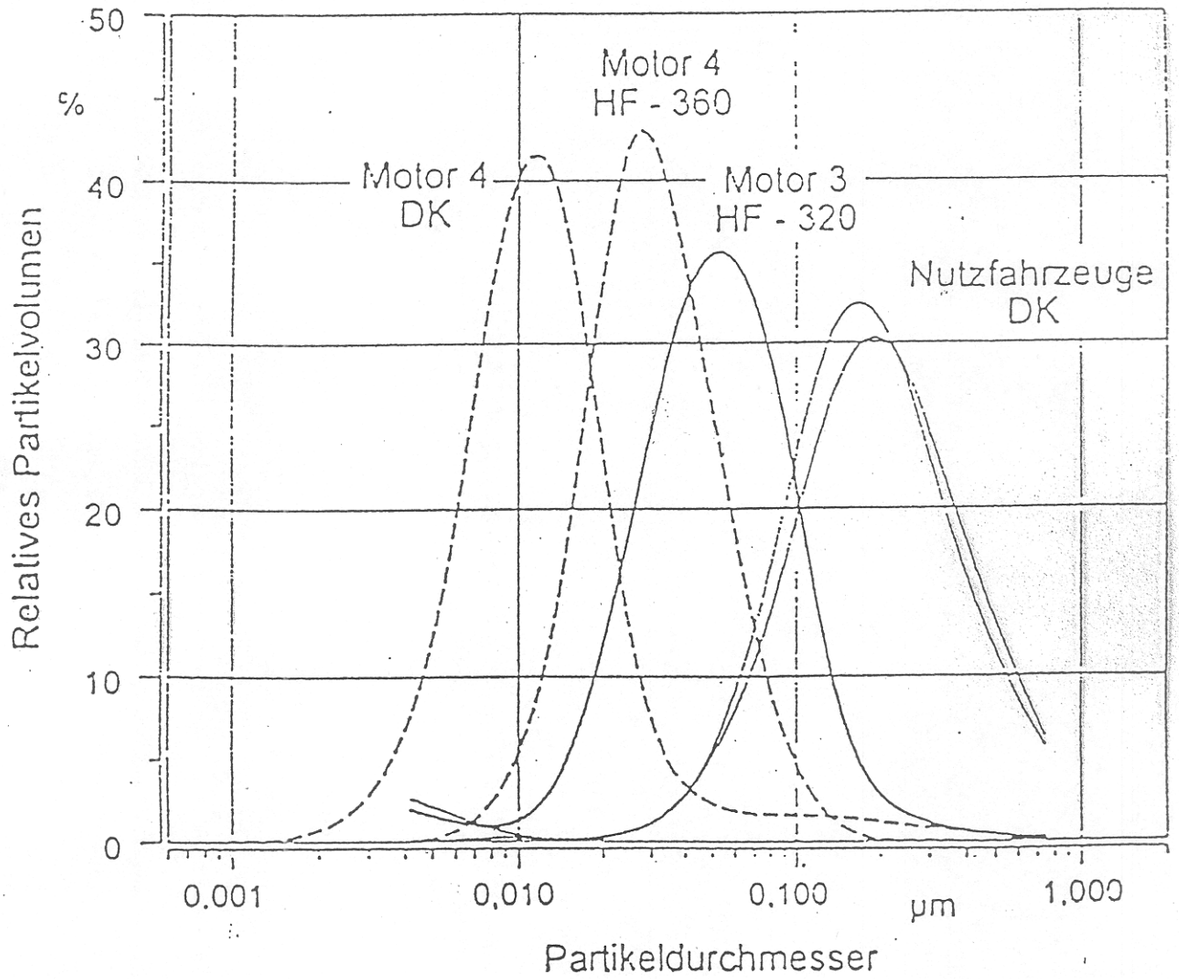
# Anzahlkonzentration bei einem direkteinspritzenden Ottomotor




Quelle: Kittelson/Universität Minnesota, 1998/1999

| | Ruß (in Form und Größe unterschiedliche Teilchen) | | | Kohlenwasserstoffe sublimiert, kristallisiert | kondensiert |
|---|---|---|---|---|---|
| organische "Partikeln" | | | | | |
| anorganische "Partikeln" | Aschen von Öladditiven | Rostpartikeln Salze (Sulfate) | Metallspäne | keramische Fasern | Wasser |

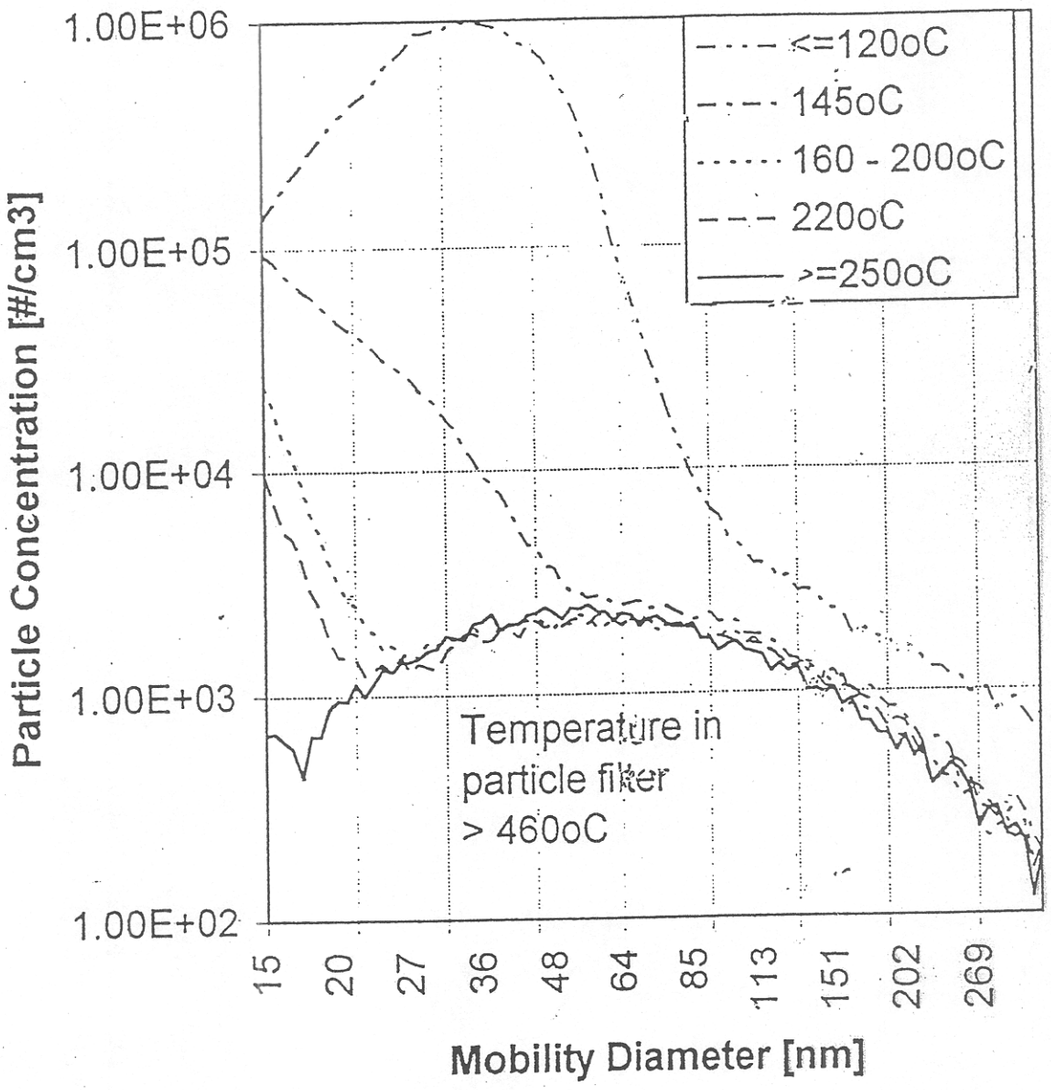
# Grössenverteilung von Russpartikeln aus Dieselmotoren mit unterschiedlicher Zylindergrösse, Drehzahl und Kraftstoff




Quelle: Mollenhauer, MTZ

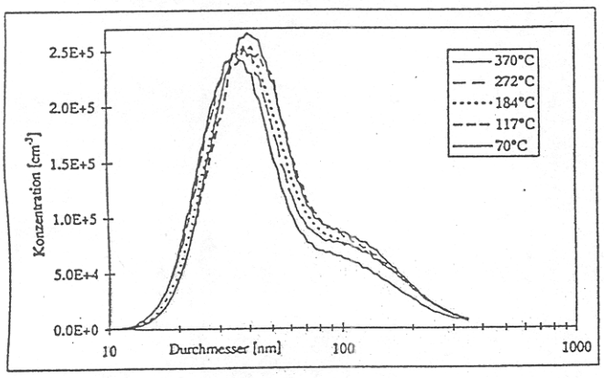
## *Diesel-Particles downstream of Trap*

Size Distribution influenced by Heating Temperatures
Size Distribution influenced Heating

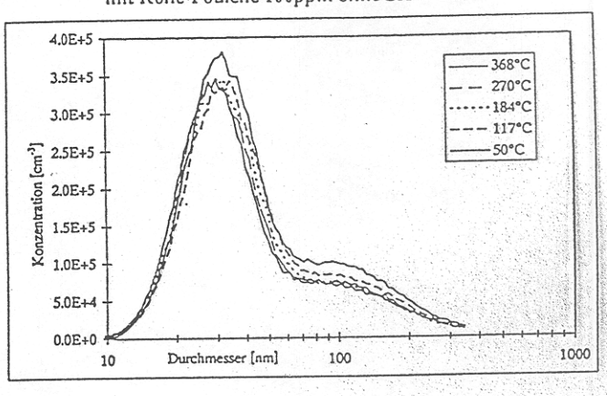


# Additives form Small Ash Particles in the whole Engine Map

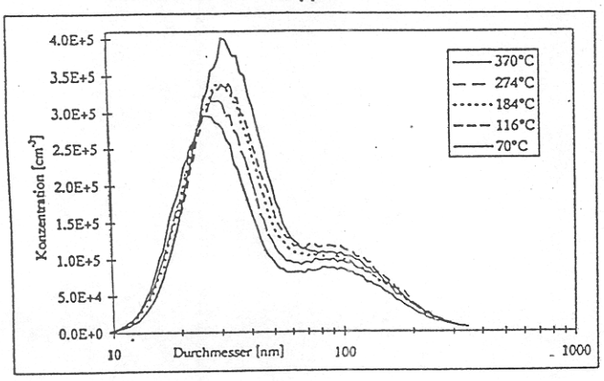
Liebherr I
Messungen bei 2000min$^{-1}$ / Vollast
mit Rône-Poulenc 100ppm ohne SHW-Filter



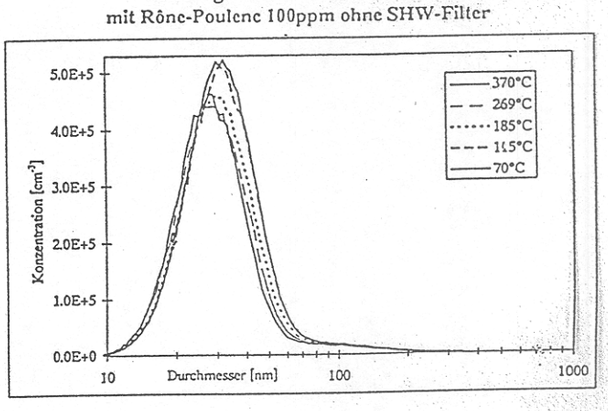

Liebherr I
Messungen bei 1400min$^{-1}$ / Vollast
mit Rône-Poulenc 100ppm ohne SHW-Filter

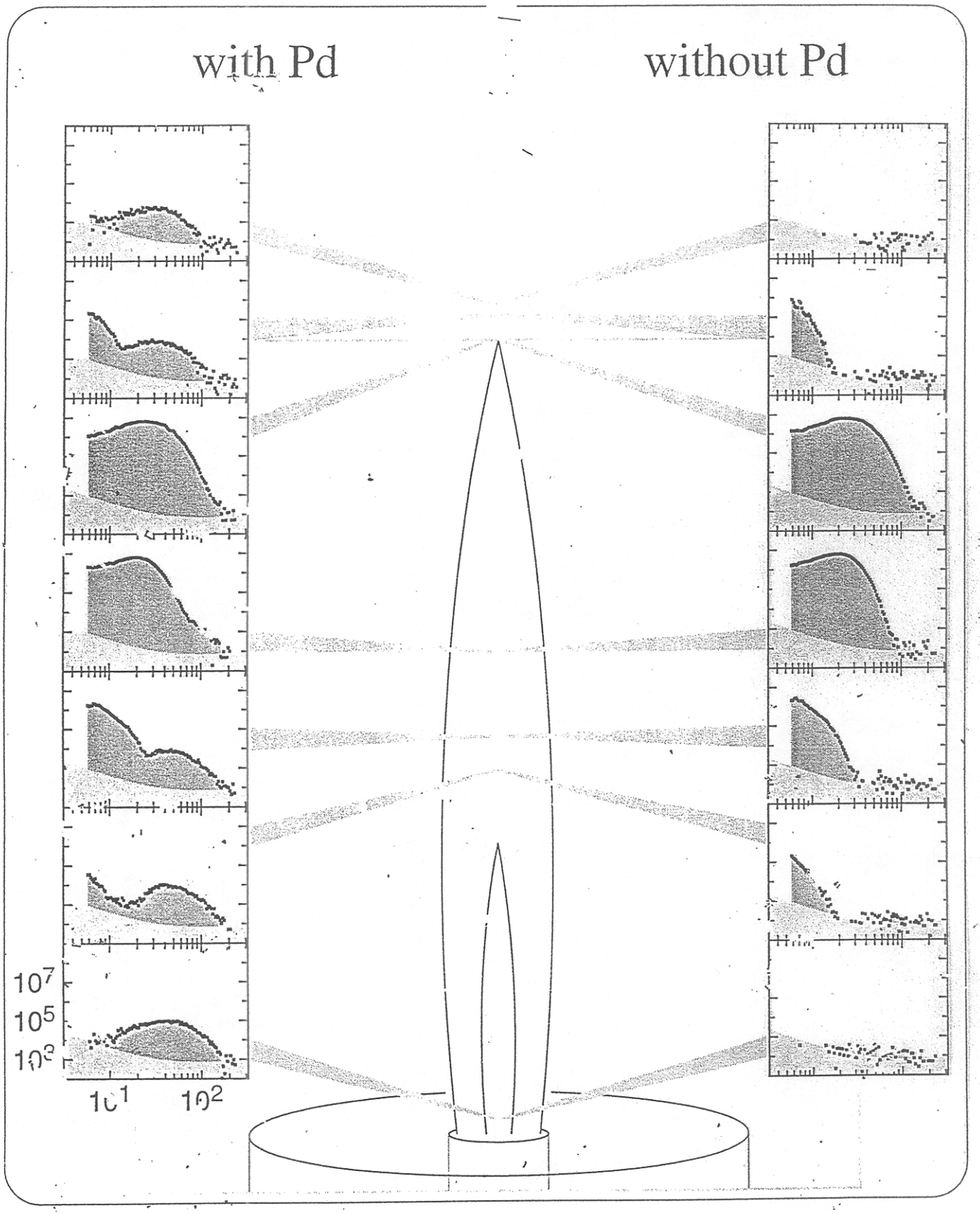



Messungen bei 2000min$^{-1}$ / 252Nm
mit Rône-Poulenc 100ppm ohne SHW-Filter

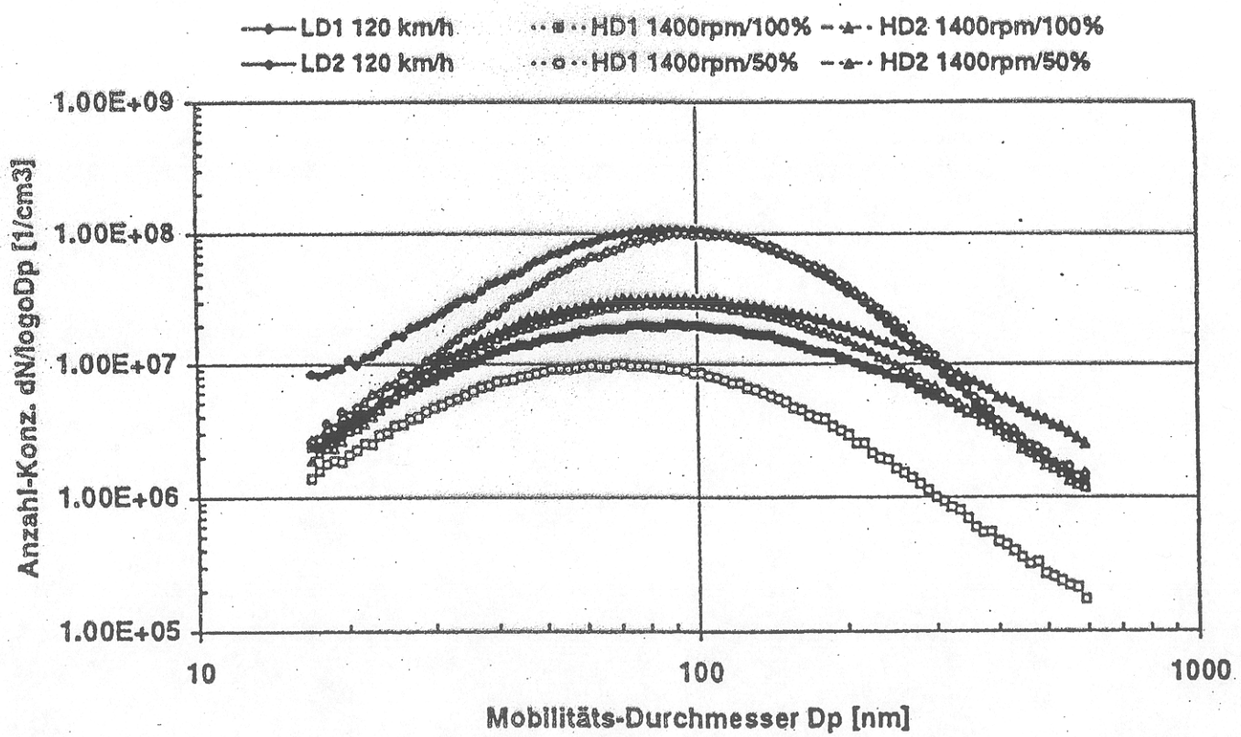



Messungen bei 1400min$^{-1}$ / 297Nm
mit Rône-Poulenc 100ppm ohne SHW-Filter




with Pd
without Pd
$10^7$
$10^5$
$10^3$
$10^1$
$10^2$

# Grössenverteilung von Dieselrusspartikeln bei 2 Nutzfahrzeugen und 2 PKW-Motoren



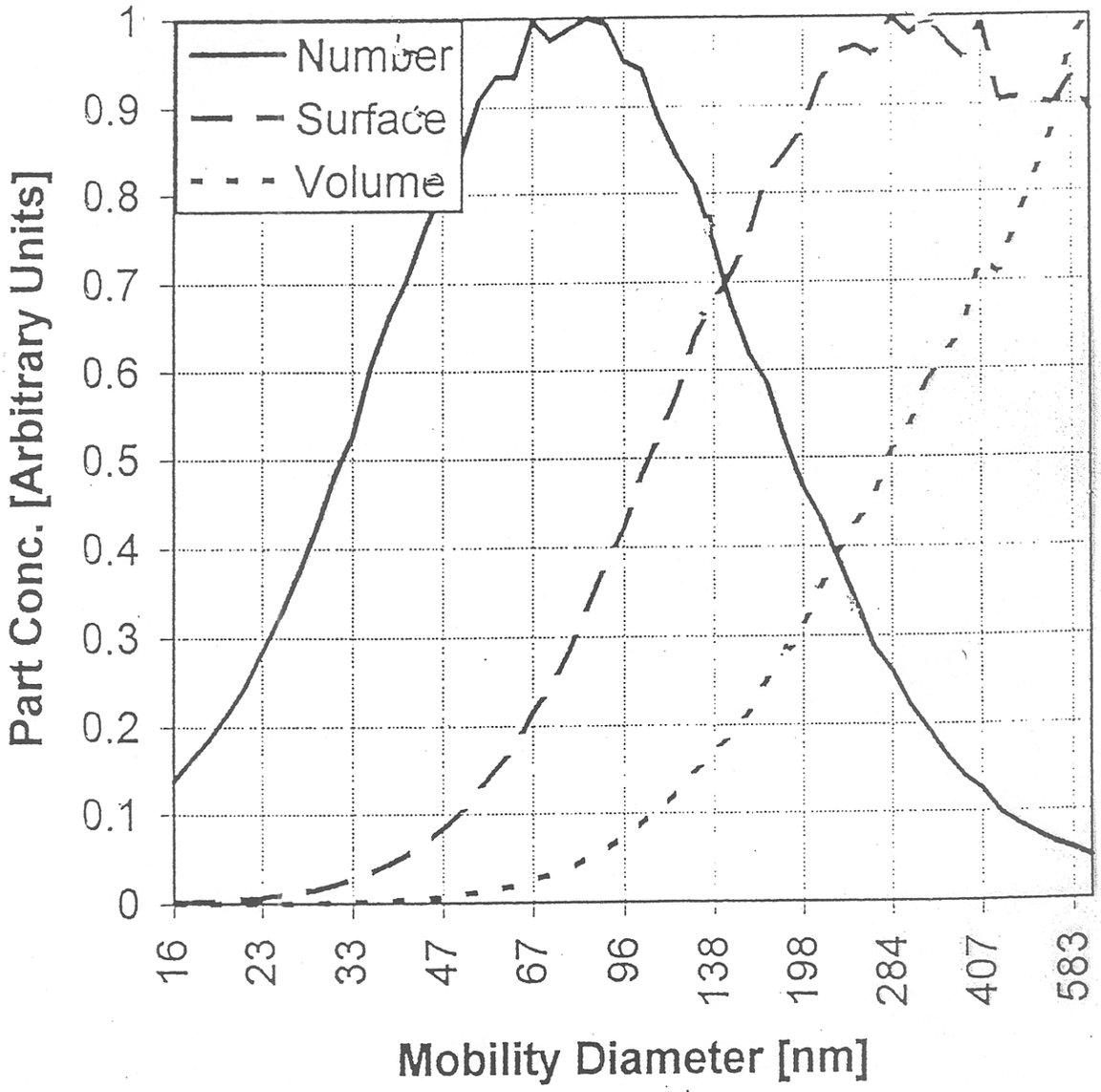

Quellev VERT

***Particle Number?***

***Particle Mass?***

***Particle Surface?***

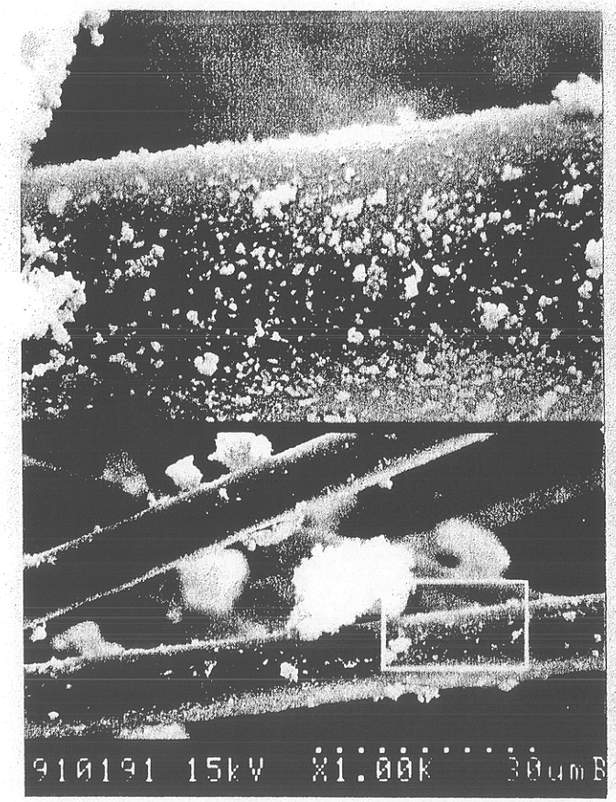
***Which has Priority?***

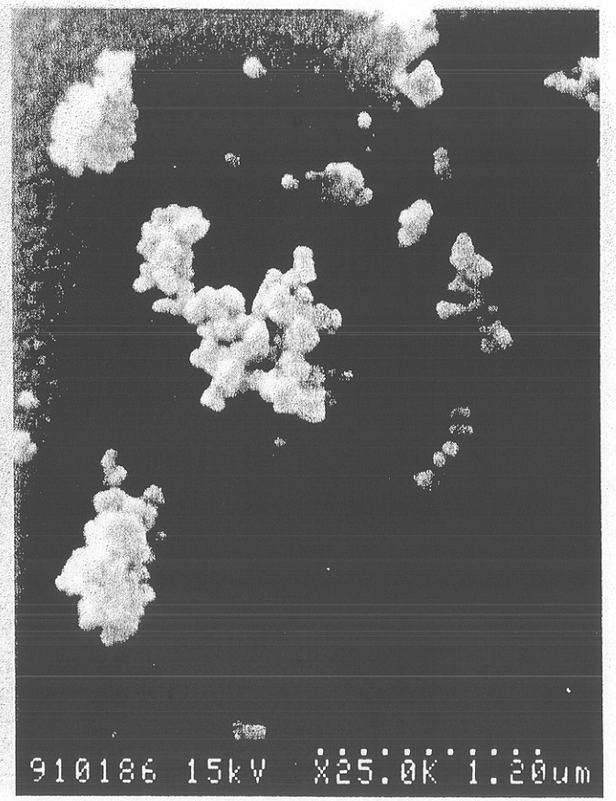


# Wie fein sind Feinstpartikel?

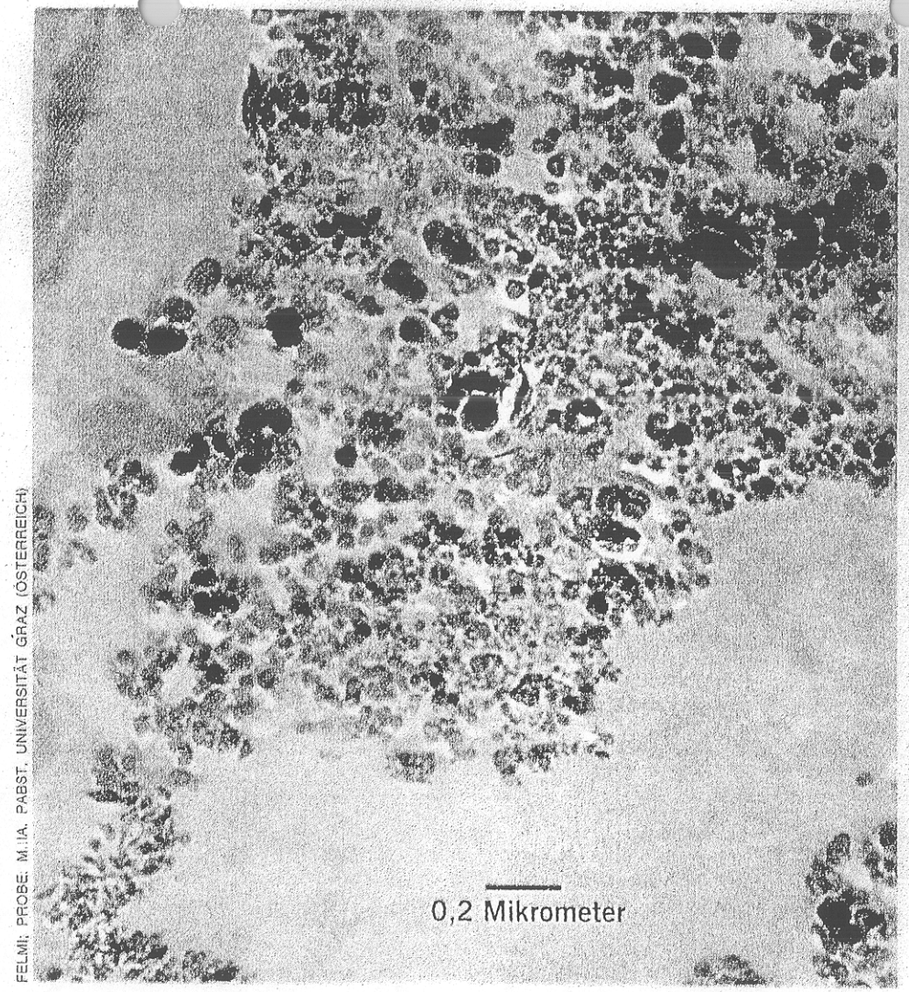
| | Durchmesser in [mm] | Sinkgeschwindigkeit [mm/s] | Sinkzeit [Std./m] | Diffusisonsweg [mm/s] | Oberfläche pro Einheitsgewicht | Zahl pro Einheitsgewicht |
|---|---|---|---|---|---|---|
| Sandkorn grob | 1 | | | | | |
| Alveole (Lungenbläschen) | 0.1 | | | | | |
| TSP / Schwebestaub | 0.057 | 100 | 0.003 | | | |
| Haar (feinstes) PM10 | 0.01 | 3 | 0.09 | $1.7 \times 10^{-3}$ | 1 | 1 |
| Zelle (kleinste) PM1 | 0.001 | 0.035 | 7.9 | $5.9 \times 10^{-3}$ | 10 | 1‘000 |
| Licht (Sichtbarkeitsgrenze) | 0.0004 | | | | | |
| Dieselpartikel (mittlere Grösse) | 0.0001 | $8.6 \times 10^{-4}$ | 322.9 | 0.03 | 100 | $1 \times 10^{6}$ |
| Virus (klein) | 0.00001 | | | | | |
| Gasmolekül (gross $SO_2$) | 0.000001 | | | | | |

# Abscheidung von Russpartikeln an Filterfasern (Faserdurchmesser µm) mit abgescheidenen Feinpartikeln um 100 nm und sehr grossen dendritisch aufgebauten Agglomeraten



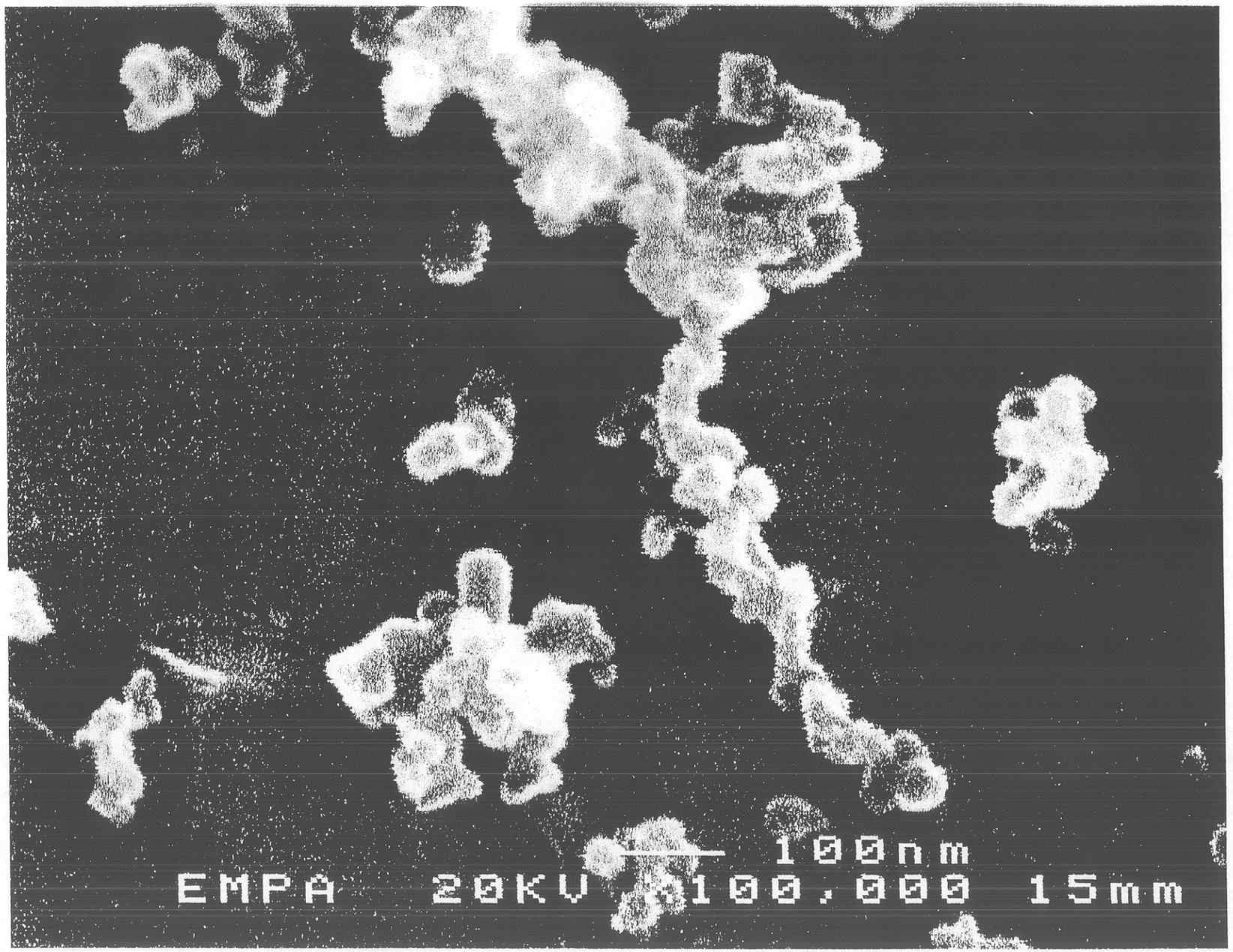



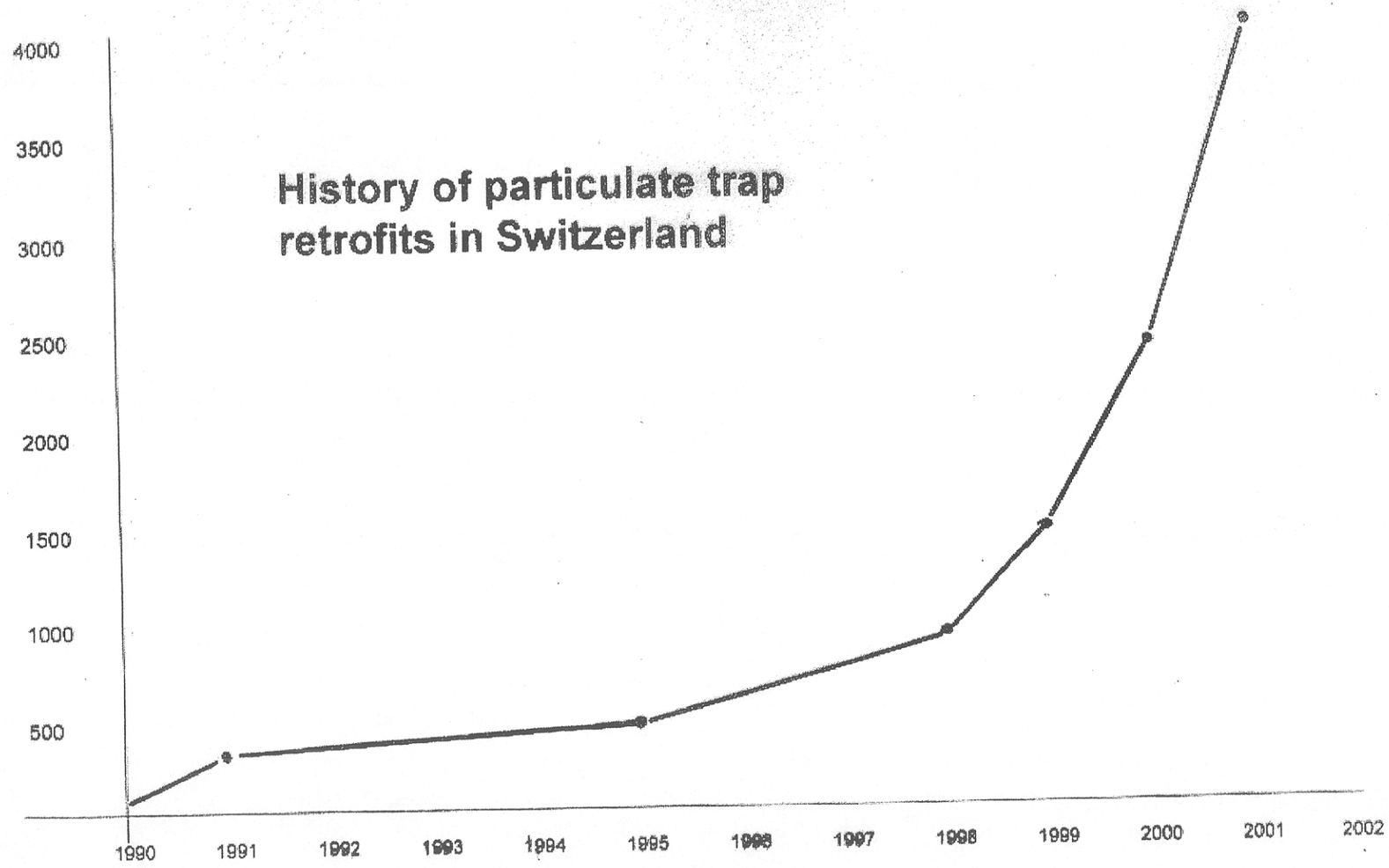

Quelle: J. Mayer, ETHZ




FELMI; PROBE. M.IA. PABST. UNIVERSITÄT GRAZ (ÖSTERREICH)

*Bild 7: In den Ötztaler Alpen wurde 1988 eine 5000 Jahre alte Gletscherleiche gefunden, die als „Ötzi" zu großer Bekanntheit gelangte (Spektrum der Wissenschaft, Juli 1992, Seite 82). In der Lunge entdeckte man schwarze Ablagerungen, deren genaue Analyse Auskunft über die damalige Lebenssituation des Gletschermanns geben kann. Die TEM-Aufnahme (links) zeigt einen Ultradünnschnitt durch Lungengewebe, das der Leiche mittels Biopsie entnommen wurde; die dunklen Teilchen sind Rußpartikel. Das RGB-Bild kombiniert die Verteilungsbilder für Kohlenstoff (rot), Silicium (grün) und Phosphor (blau). Die häufigste Komponente ist der aus nanometergroßen Teilchen bestehende Ruß (rot). Darin eingebettet sind siliciumreiche Muskowit-Partikel (grün), die man bei konventioneller TEM übersehen hätte. Außerdem findet sich Calciumphosphat (blau). Die EFTEM-Analyse enthüllte im Lungengewebe noch weitere Mineralpartikel, die der Gletschermann zu Lebzeiten inhalierte.*


100nm
EMPA 20KV x100,000 15mm


History of particulate trap retrofits in Switzerland
4000
3500
3000
2500
2000
1500
1000
500
1990
1991
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002

| Systèmes de filtre [2] Condition pour l'intégration des filtres dans la présente liste: avoir passé avec succès le test d'adéquation (5.2) selon les critères du cahier des charges VERT (5.1) | Tests [1] | | Champs d'utilisation | | | | | | Expériences | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Test d'adéquation à l'état neuf | Test d'adéquation après utilisation | Voitures | Camions | Autobus | Engins de chantier | Elévateurs | Moteurs stationnaires | Durées d'utilisation maximales (heures de service) | Nombre de systèmes en fonction |
| **OBERLAND-MANGOLD** | | | | | | | | | | |
| Filtre à fibres tricotées | | | | | | | | | | |
| • R: additif de carb. satacen (Fe) [3] | • | | | • | • | • | • | • | > 10'000 | >2000 |
| Filtres à fibres spiralflow | | | | | | | | | | |
| • R: additif de carb. DFX-DPF [4] | • | | | • | • | • | • | • | | |
| **UNIKAT** | | | | | | | | | | |
| Filtre cellulaire céram. CORNING | | | | | | | | | | |
| • R: régén. électrique à l'arrêt à bord | • | • | | • | | • | • | • | 25000 | >7000 |
| • R: filtre interchang. (régénération ext.) | | | | | | • | • | | | |
| **DCL** | | | | | | | | | | |
| Filtre cellulaire céramique IBIDEN | • | | | | | • | • | • | ? | ? |
| • R: additif de carb. satacen (Fe) [3] | • | | | | | • | • | • | | |
| • R: filtre interchang. (régénération ext.) | | | | | | | | | | |
| **AMMANN** | | | | | | | | | | |
| Filtre à fibres tricotées BUCK | | | | | | | | | | |
| • R: add. de carb. DFX-DPF (Ce/Pt)[4] | • | | | | | • | | | ? | ? |
| Filtre à fibres tricotées KANY | | | | | | | | | | |
| • R: additif de carb.DFX-DPF(Ce/Pt)[4] | • | | | | | • | | | | |
| **INTECO** | | | | | | | | | | |
| • R: additif de carb.: satacen [3] | • | | | | | • | | | ? | ? |
| • R: revêtement catalytique | | | | | | | | | | |
| **GREENTOP** | | | | | | | | | | |
| • R: additif de carb.: satacen [3] | • | | | | | • | | | ? | ? |

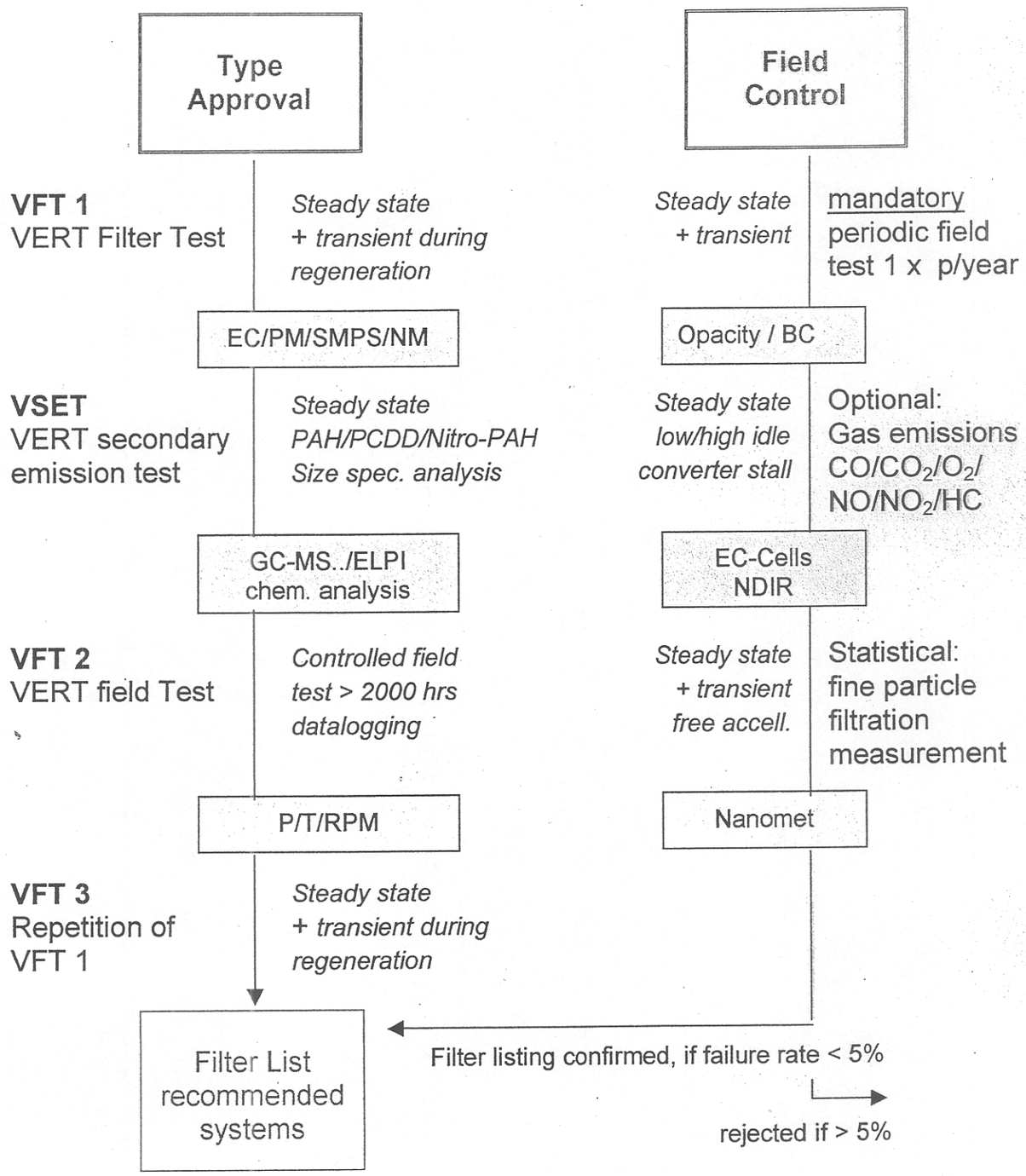
[1] • | • Résultat positif pour les deux parties du test d'adéquation complet (état neuf et après utilisation)
- Tous les autres cas sont assortis de réserves.

[2] Les systèmes de filtre doivent être définis et marqués de manière univoque dans leur équipement technique.

[3] L'emploi d'additifs de carburants n'est admis qu'en liaison avec des dispositifs automatiques de dosage «on-board»

[4] Cet additif n'est pas encore admis en Suisse.

# Verification Tests and Control Schemes for Diesel Particulate Filters in Switzerland



# Trap-System Specification

- Filtration rate for Particulate Mass desirable > 80 %
- Filtration rate for Particle Number mandatory > 95 %
- Filtration rate for EC-Mass mandatory > 90 %
  For the fresh, loaded and regenerated trap
  the new and old trap (old = 2000 hrs of field operation)
  also transient during regeneration

- No increase of any other toxic emissions
  CO, HC, NO, $NO_2$, $N_2O$
  Sulfates (desirable)
  PAH, Nitro-PAH, PCDD/F
  Heavy metals in any form

- Pressure loss for loaded trap < 200 mbar
  New traps should unloaded be below 50

- Automatic dosing systems for fuel additives

- Electronic OBC with 2 alarm levels for
  trap clogging (2 stages orange/red) and trap damage

- Field refuse criterion: < 10 % opacity (future 5 %)
  Equivalent 0,24 1/m and 0,033 g/m$^3$
  during snap acceleration (low to high idle)

- Cost < 100 SFr./kW (future < 50 SFr/kW)

- Noise, Safety, Size, Heat radiation

- Investment, maintenance cost, Service Interval

- + + + + + see Filter List

# Swiss Legislation / Regulations 2001

*"Diesel soot particles are carcinogenic and must therefore be minimized acc. to BAT"*

- BUWAL (Swiss Environnement Protection Agency)
  requires traps for Diesel at construction sites
  In or closeby cities
  Implementation by local government (Cantons)
  only VERT-certified trap-systems recommended
  periodic field control required (yearly)
  exceptions for very short operation period (weeks)
  in force 1998
  http://www.buwal.ch/projekte/luft/partikelfilter/e/index.htm

- SUVA (Swiss Occupational Health Authority)
  requires traps for underground work
  and all closed or semi-closed rooms
  100 % application, no exceptions
  only VERT-certified traps are accepted
  in force 2000
  http://www.suva.ch

- Trap systems must comply with other legislation
  (noise, safety)
  in force 1990/95

- Trap systems using catalytic coatings or fuel catalysts
  must prove "no emission of secondary toxic emissions"
  In force 1990

| | Gases | | | | Aerosols [5] | |
|---|---|---|---|---|---|---|
| $mg/Nm^3$ | CO | NO | $NO_2$ | $SO_2$ | PM = EC + OC | $H2SO_4$ |
| Emissions | 1000 | 2700 | 300 [1] | 100 | 250 [2] | 25 [6] |
| Immission Limits | | | | | | |
| Switzerland | 35 | 30 | 6 | 5 | 0.2 (TC) [3] | 1 |
| Germany | | | | | 0.1 (EC) [4] | 1 |
| MSHA 1998 | | | | | 0.16 prop. | |
| MSHA 2003 | | | | | 0.05 prop. | |
| Dilution required | > 28 | > 90 | > 50 | > 20 | > 1000 | > 25 |

[1]) fraction $NO/NO_2$ estimated
[2]) about 80 $mg/Nm^3$ carbon particulates
[3]) Total carbon = elementary carbon (EC) + organic carbon (OC)
[4]) Elementary carbon as per TRGS 554, status 1997
[5]) settling velocity < 1.25 m/s / 50% / size < 5 µm
[6]) SAE 1999-01-0116

$$\text{Required Dilution} = \frac{\text{Emission}}{\text{Imission Limit}} \rightarrow \text{Priority}$$

# Partikelemissionen in der Schweiz und Kalifornien

| Schweiz | Gesamt | Onroad | | Offroad | |
|---|---|---|---|---|---|
| | t/a | t/a | % | t/a | % |
| 1990 (49) | | 2600 | 50 | 2600 | 50 |
| 1990 (49+) | | 2615 | 50.3 | 2582 | 49,7 |
| 1995 (49+) | | 2096 | 44.9 | 2577 | 55.1 |
| 2000 (49) | | | 40 | | 60 |
| 2000 (49+) | | 1574 | 37,9 | 2576 | 62,1 |
| 2010 (49) | | | 30 | | 70 |
| 2010 (49+) | | 548 | 19 | 2332 | 81 |
| **Kalifornien** | | | | | |
| 1990 | | | 42.1 | | 57.8 |
| 2000 | | | 28.8 | | 71.2 |
| 2010 | | | 23.7 | | 76.3 |

TTM 6.11.2001

# The Swiss Chronicle to reduce Diesel Particulate emissions by > 99 %

- Offroad Emissions Inventory 1993
  (computer-model for predictions now available on CD)

- VERT-Project 1994-1998 to define and prove BAT

- BUWAL (Swiss EPA):
  Clean Air Act Amendments 1998
  - Diesel Particulate classified as "carcinogen"
    (to be minimized acc. to BAT irrespective of cost)
  - PM 10 – Limit 20 µg/m3 (exceeded in all cities)
  - Traps for construction sites in/nearby cities

- SUVA (Swiss Occupational Health Authority):
  Traps mandatory for the working place 3/2000

- Implementation Tools:
  - Trap-system specification 1996
  - Trap-system-verification protocol 1997
  - Filter-list of all verified traps on the Net 1998
  - Ultrafine particle metrology "NanoMet" 1999
  - EC-oriented calibration method CAST by EAM 1999
  - Trap OBD-systems "LogLink" 1999
  - Trap manufacturer association AKPF 1998
  - Nanoparticle measurement conference since 1997
  - BauRLL: Traps at all construction sites class B in 1 year
  - class A in 5 years

- > 4000 traps in operation – controlled by field testing

- STUMP-Postulat: "Retrofit of all swiss HDV-onroad (66'000) with efficient filters vehicles as soon as possible"
  Government decision expected in 2002

# Ergebnisse

## Partikelanzahl:

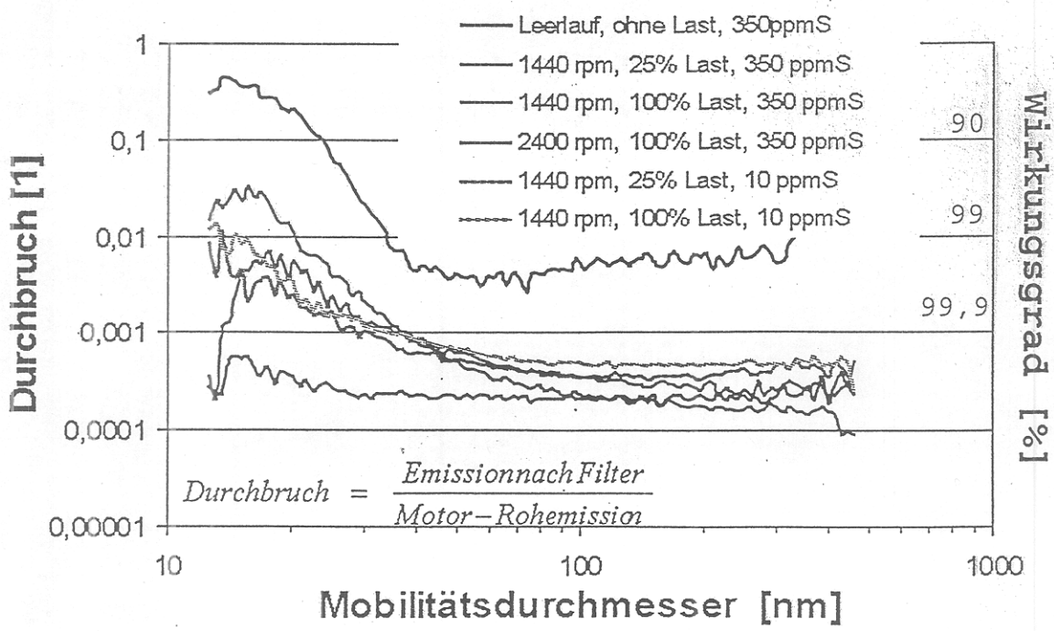



**Bild 2:** Größenverteilung des Filterwirkungsgrads

***Figure 2:*** *Size dependent efficiency and breakthrough*

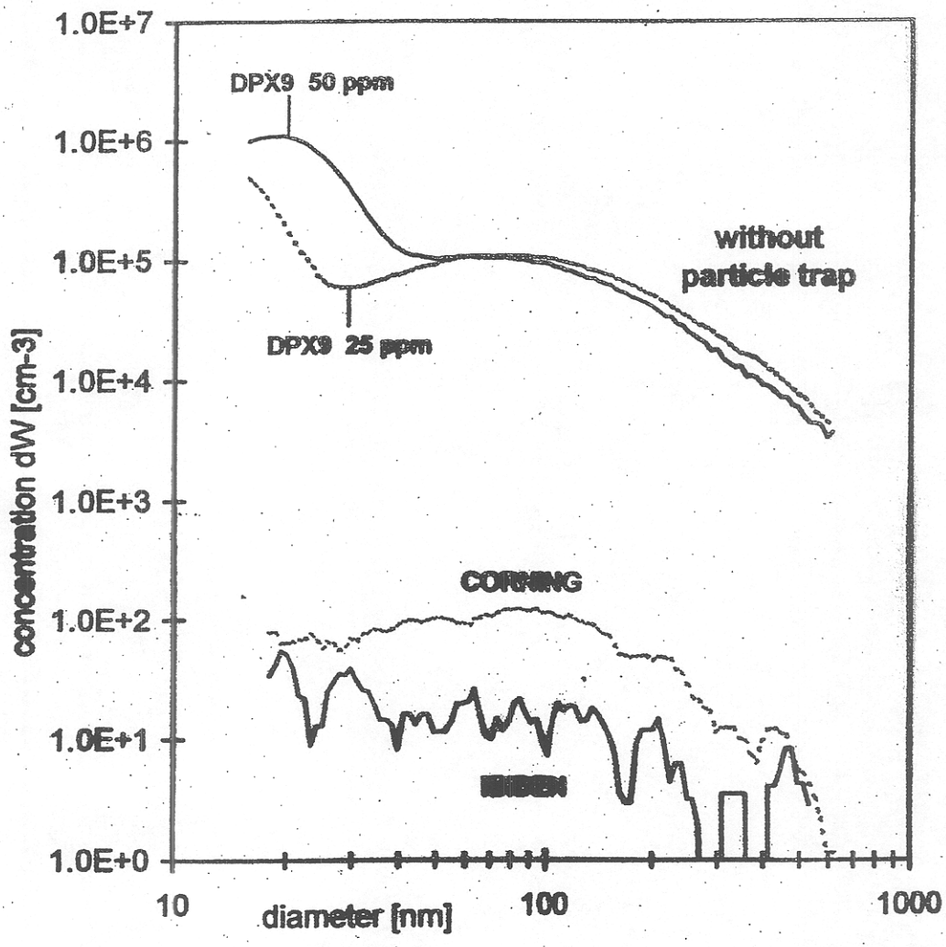
# Feinpartikel-Abscheidegrade im Grössenbereich 20 - 200 nm des SiC-Zellenfilters von IBIDEN

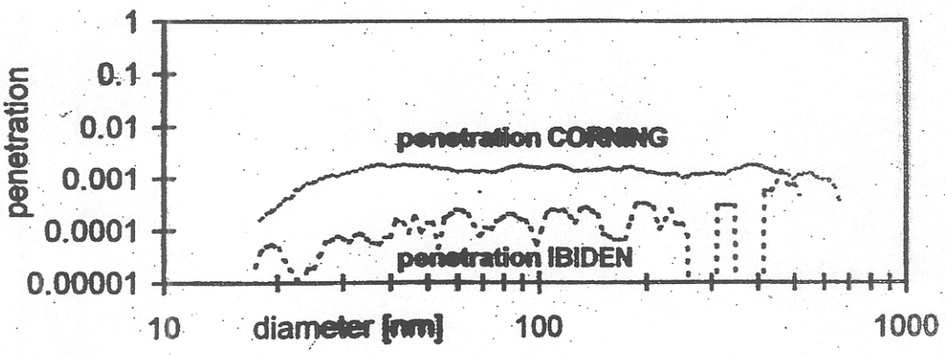
| | 2000 $min^{-1}$ Volllast | 1400 $min^{-1}$ Volllast | 2000 $min^{-1}$ 252 Nm | 1400 $min^{-1}$ 297 Nm |
|---|---|---|---|---|
| Filter A1neu | 99.99 | 99.98 | 99.90 | 99.99 |
| Filter A1 | 99.97 | 99.98 | 99.99 | 99.98 |
| Filter A1 | 99.98 | 99.99 | 99.99 | 100.00 |
| Filter B1 neu | 99.98 | 99.97 | 99.91 | 100.00 |
| Filter B1 | 100.00 | 99.99 | 100.00 | 99.99 |
| Filter B1 | 100.00 | 100.00 | 100.00 | 100.00 |
| Filter B2 neu | 100.00 | 99.99 | 100.00 | 99.82 |

Quelle: VERT Filtereignungstest 1999

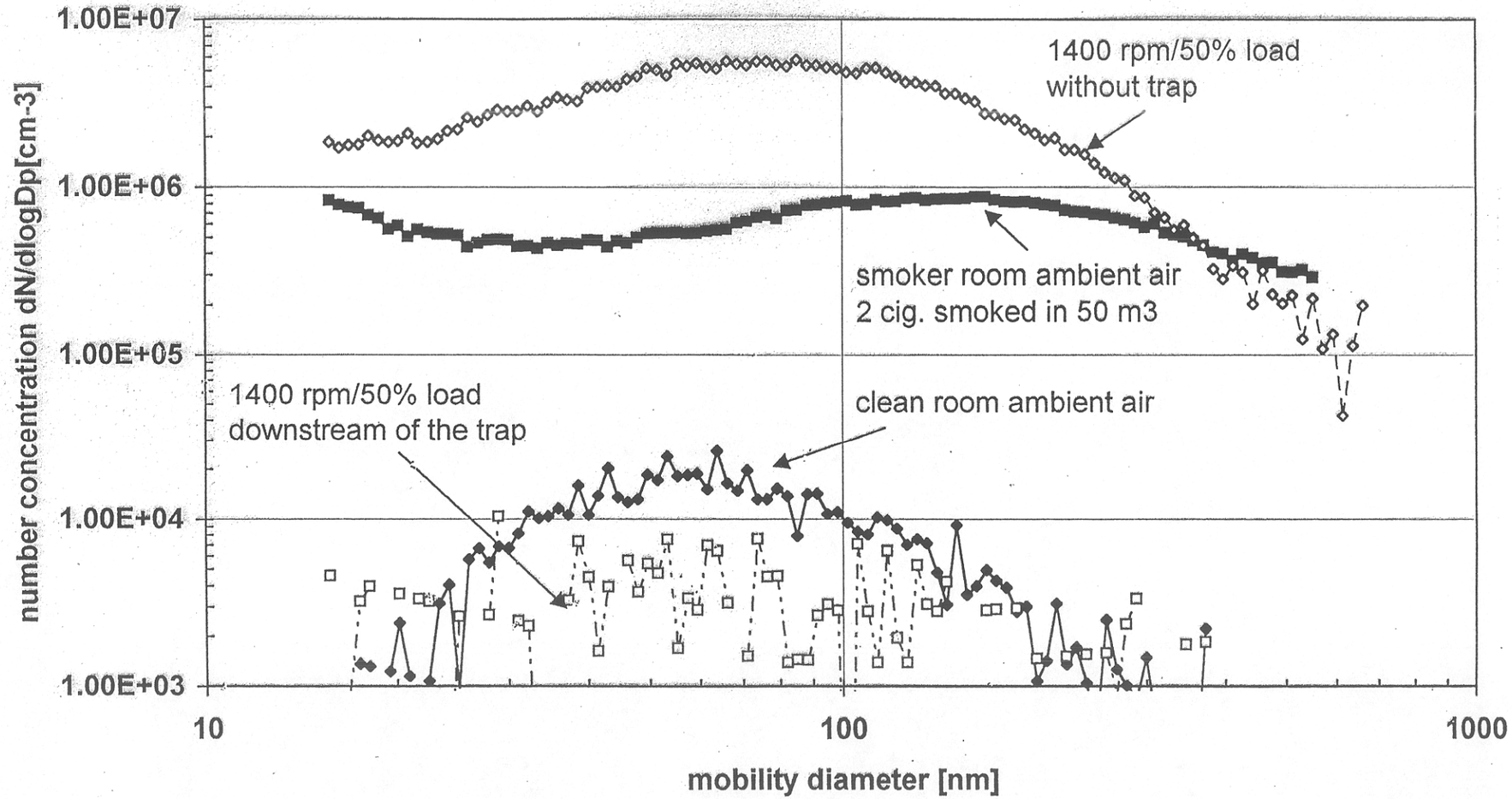
# Comparison of particle size spectra of 2 modern traps with fuel additives

Liebherr D914 T, 1400 $min^{-1}$/ full load, after reg. with thermodenuder



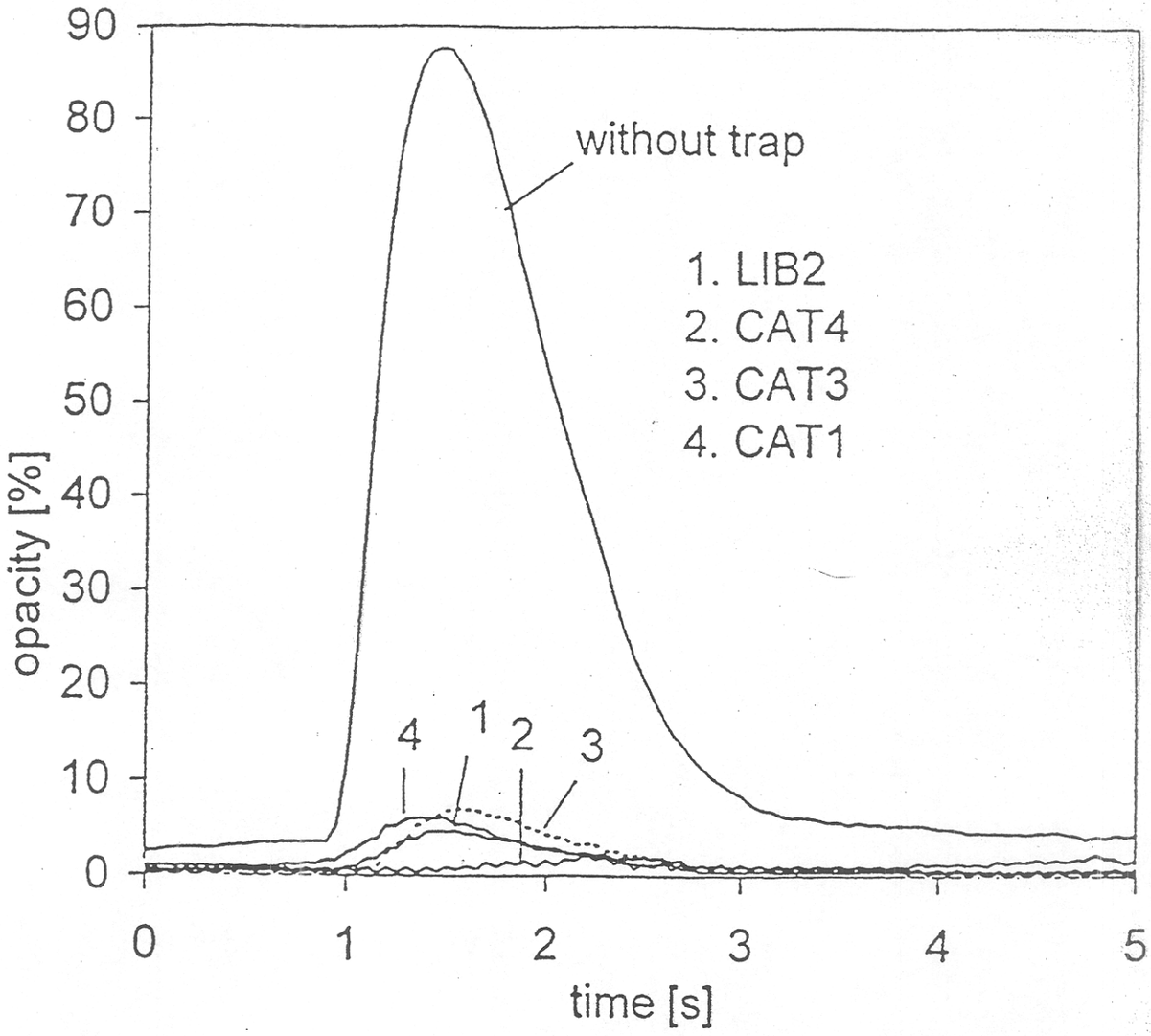
## Diesel Emissions with and without Particle Trap vs. Ambient Air Particle Concentrations



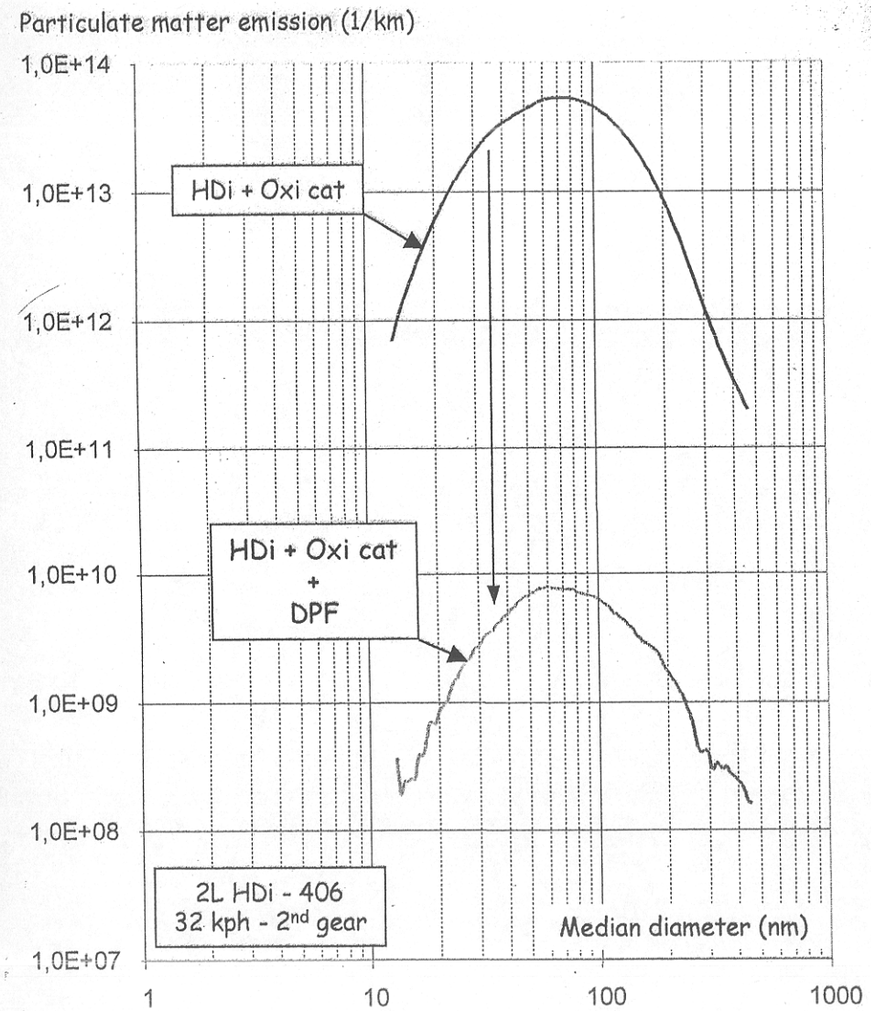

Ma, 06.05.1999, Btr6_Amb.xls, diagr. 1

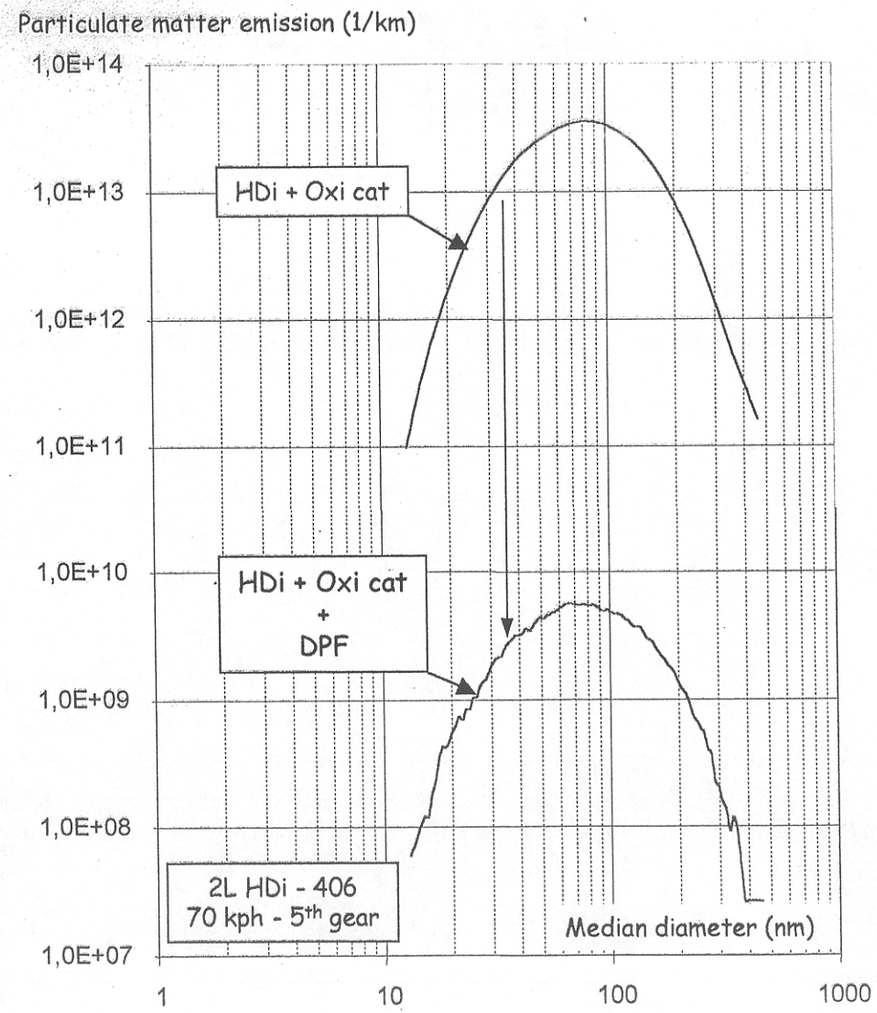
Meas. FH Biel, Liebherr 110kW TDI of 03. and 05.11.1998

# Test Cycle: Free Acceleration



# SiC FILTER REDUCTION OF PARTICULATE MATTER EMISSION ON A 406 - 2L HDi



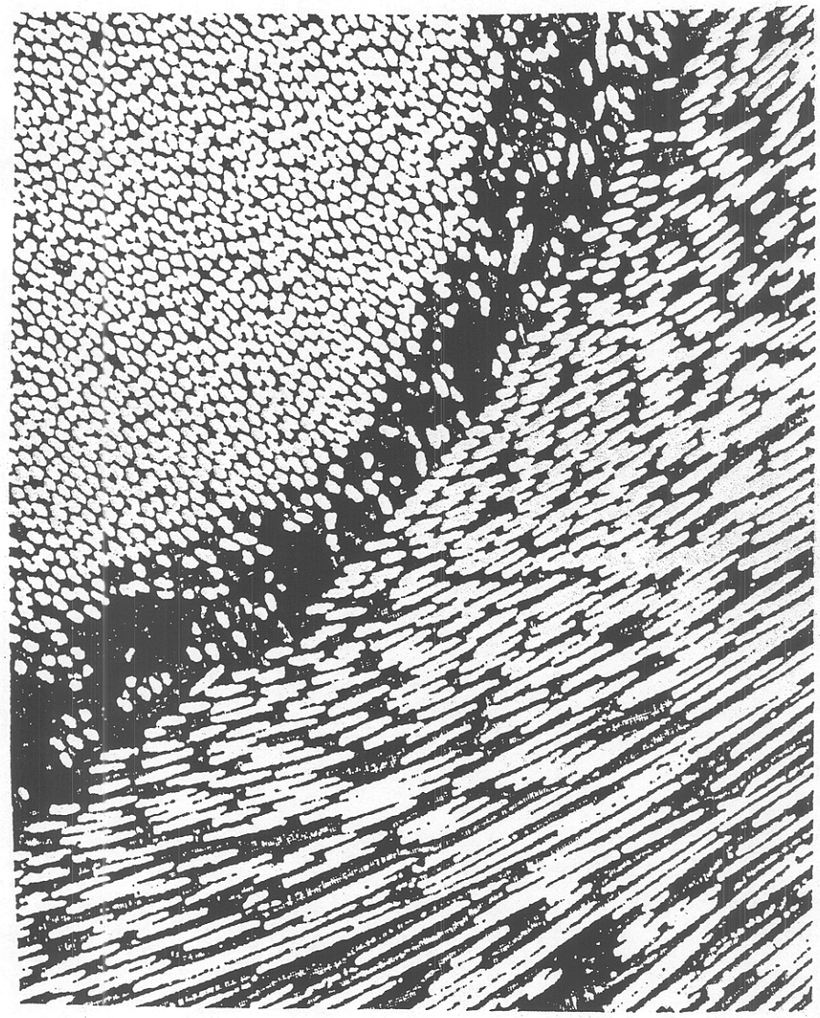



[g/kWh]
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
2000min-1
full load
1400min-1
full load
SO4
H2O
soot mass

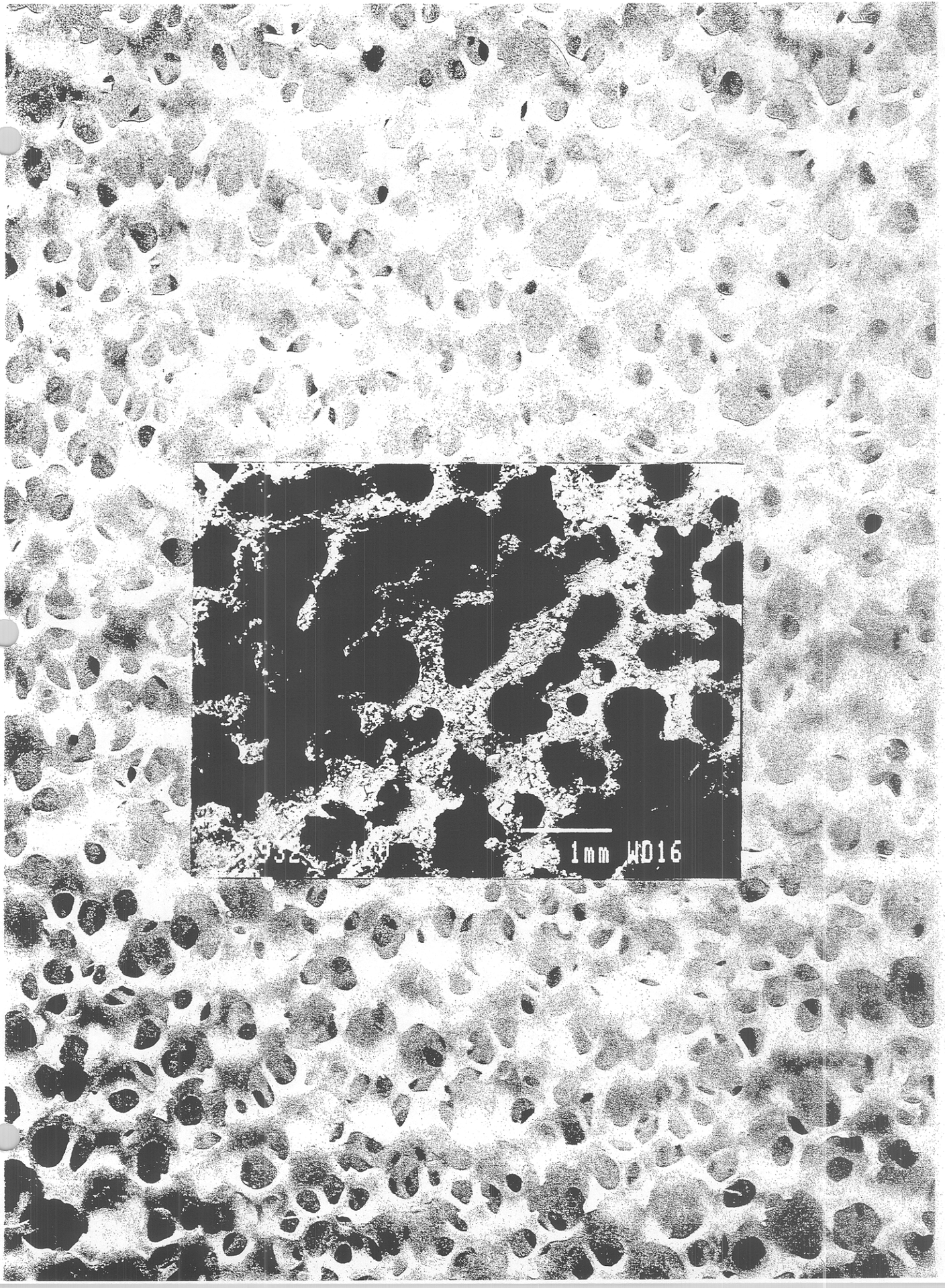
| Products | PMAG [1] | PZAG [2] | ECAG [3] |
|---|---|---|---|
| After field test 2000 hrs: | | | |
| SHW (LIB1) | 3.2 | 96.3 | - |
| SHW (CAT1) | 77.5 | 97.8 | 97.2 |
| BUCK (LIB2) | 76.5 | 95.4 | 94.0 |
| BUCK (CAT3) | 64.2 | | |
| ECS (LIB3) | 12.4 | 99.9 | 99.3 |
| UNIKAT (CAT4) | 54.7 | 99.0 | 98.1 |
| HJS/CRT | 13 | 99,9 | 98,5 |
| MC | 85.3 | 99.5 | |
| Average | | 98.3 | 96.8 |

[1] PMAG: Particulate mass based efficiency
[2] PZAG: Particulate number based efficiency
[3] ECAG: Elementary carbon based efficiency

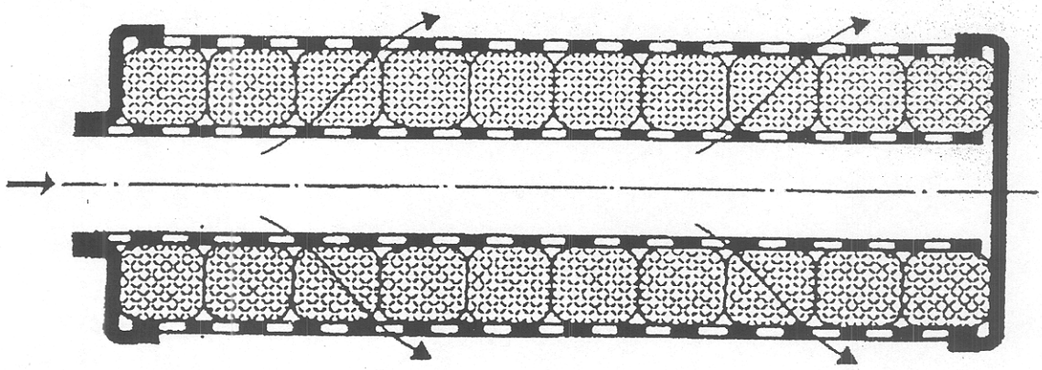
## Filtration Efficiency of Particulate Traps



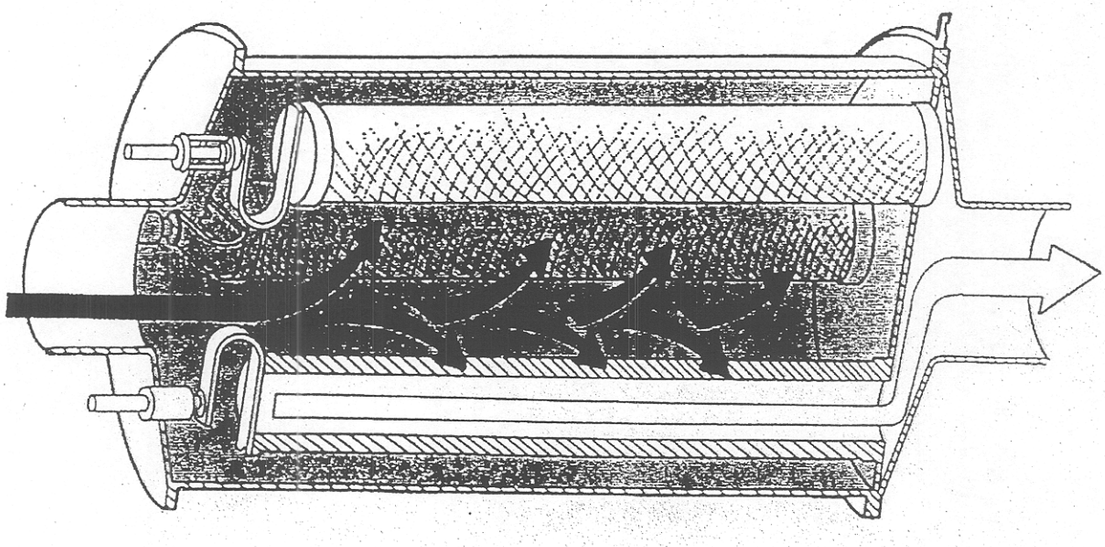
| | | |
|---|---|---|
| TTM | Faserverteilung im Knoten | HdT Essen<br>17./18.9.1996 |


1mm WD16

20kV 4X02
100µm
#0001 10-09-00
X200

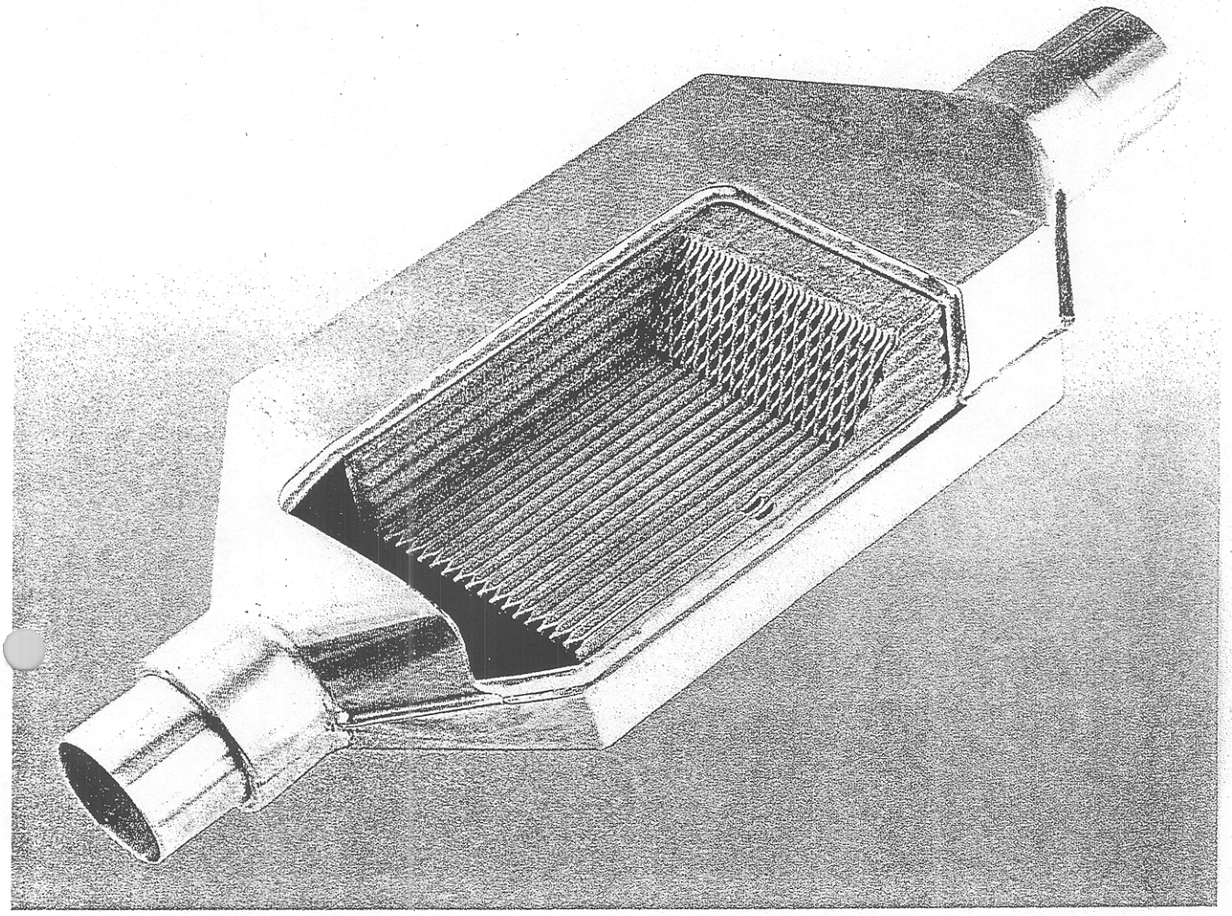


# Fasergestrick - Filterkerze



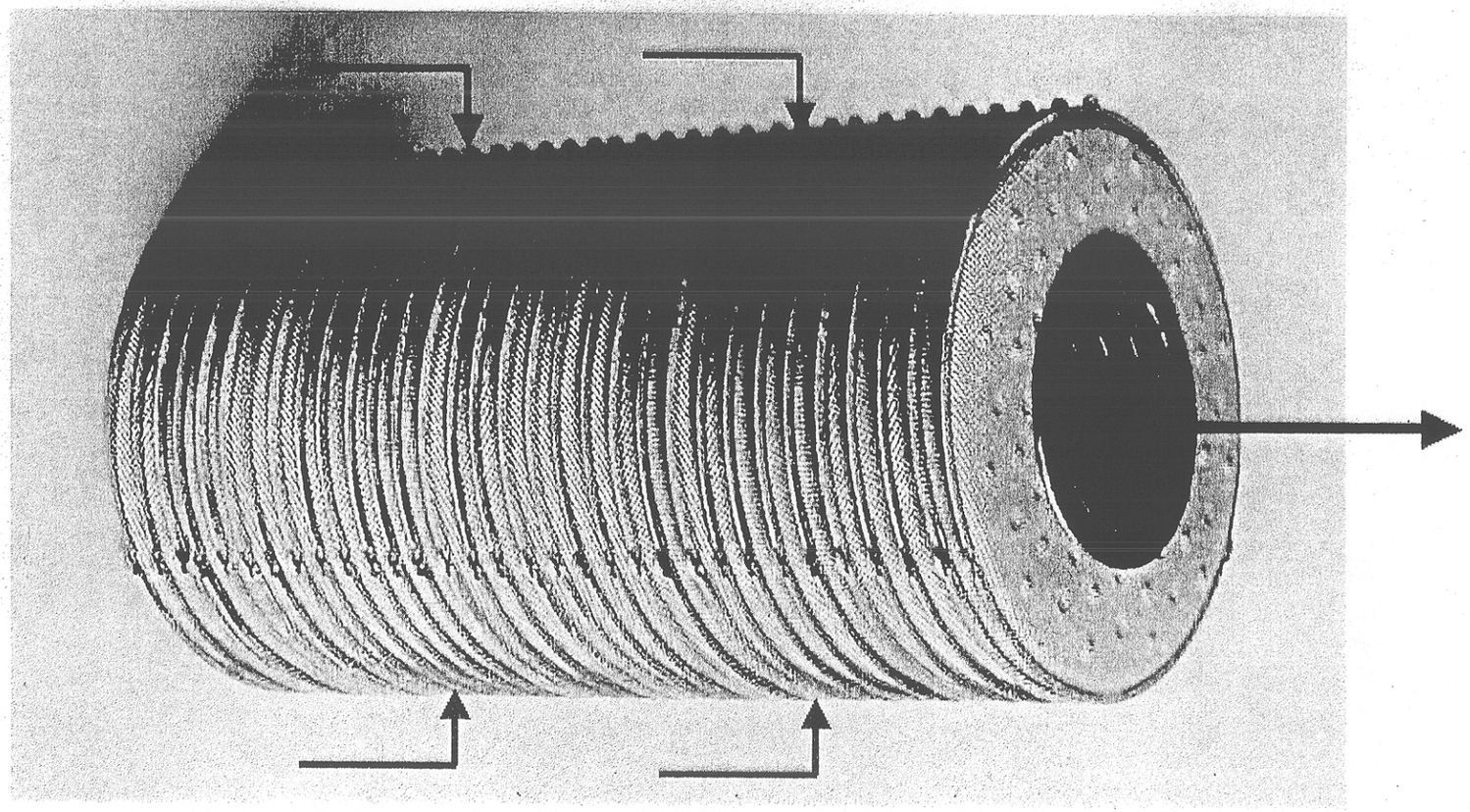
# Wickel - Filter

# Der SHW-Rußfilter für Dieselmotoren



Schon Heute Weiter SHW

PUREM



***Filter aus porösen Sintermetalltaschen***

*Taschen wechselweise am Innendurchmesser – Außendurchmesser verschweißt.*
*Große geometrische Variantenvielfalt darstellbar.*

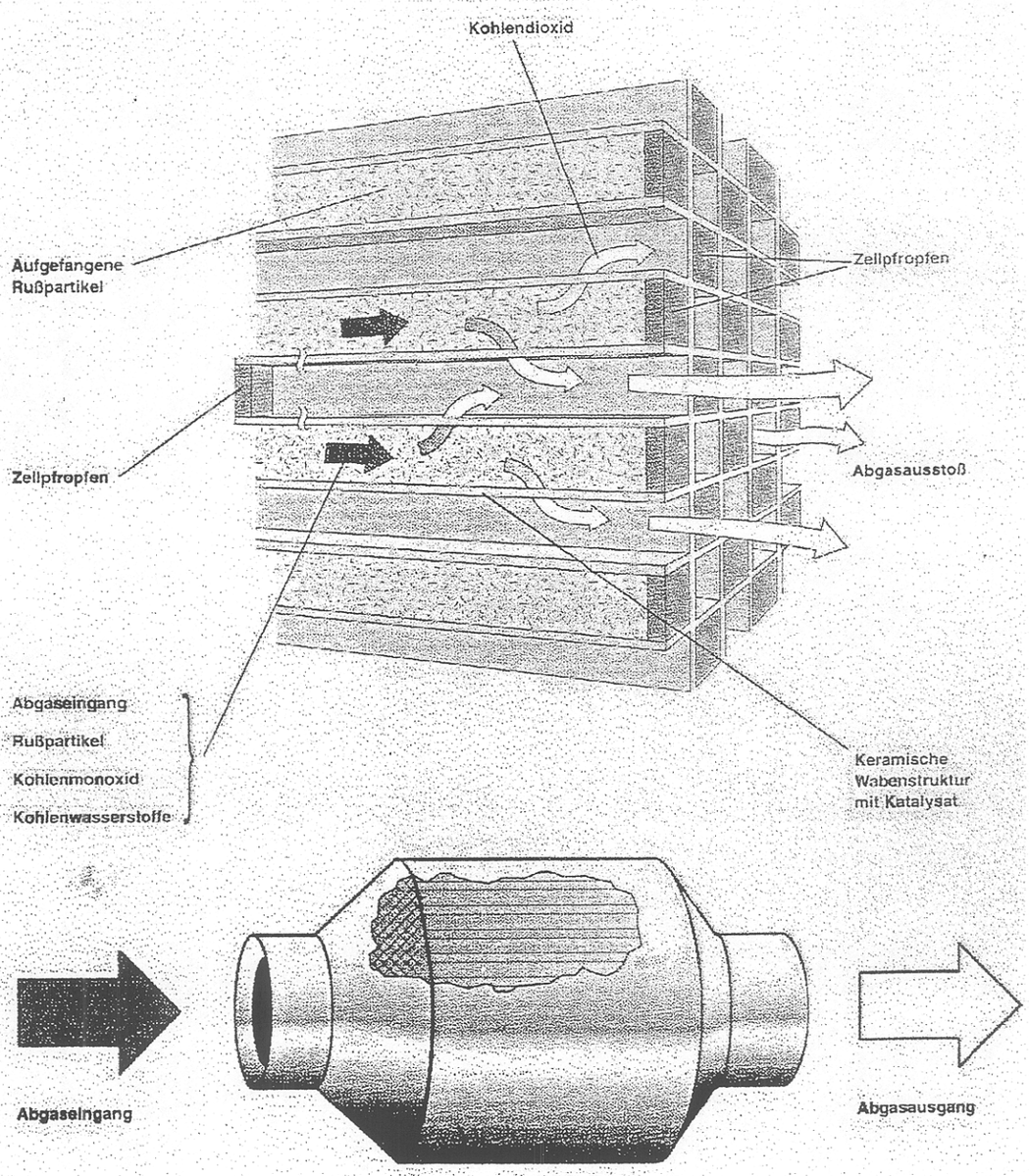
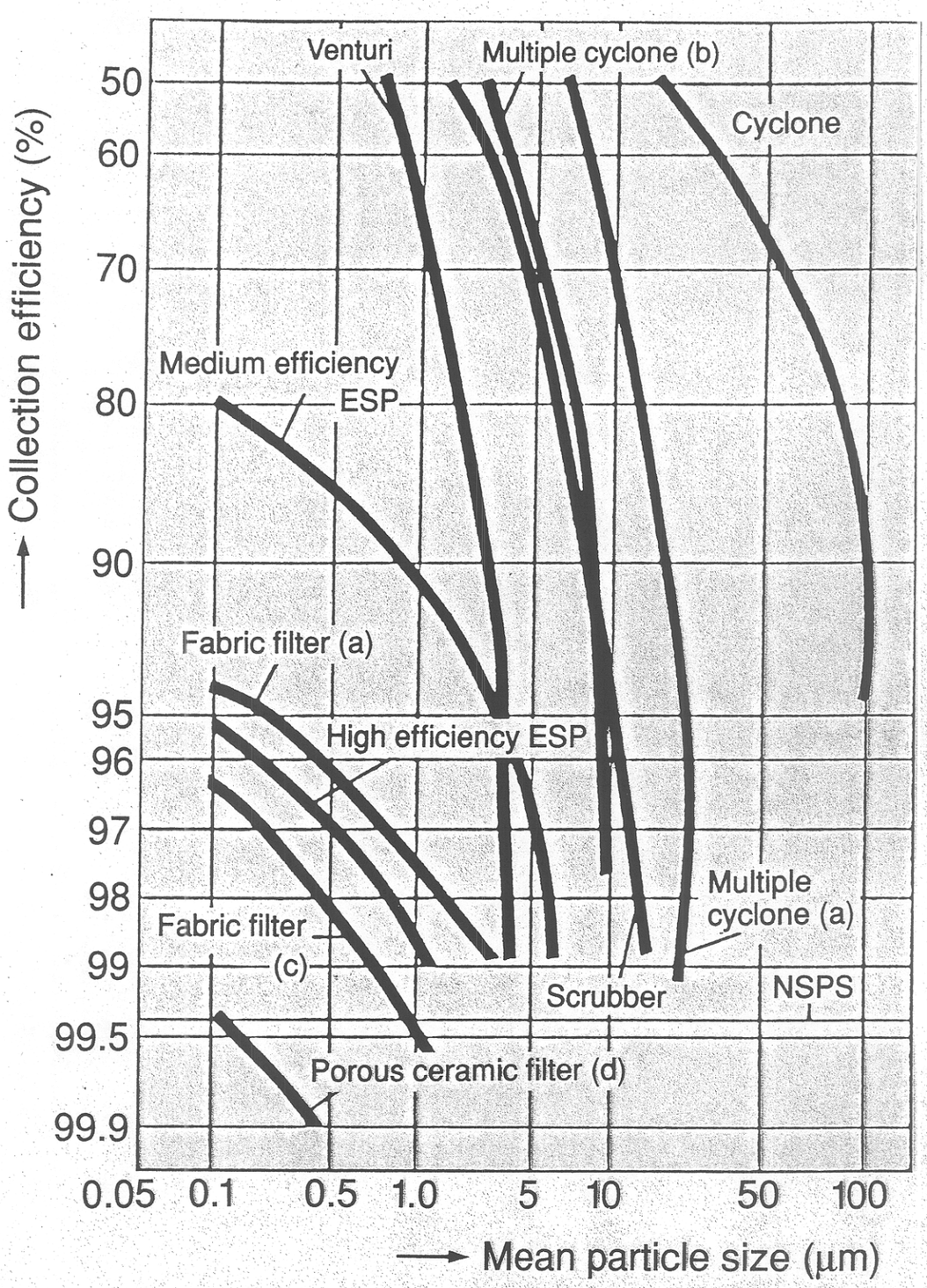



**Bild. 7. Funktionsweise DPX**

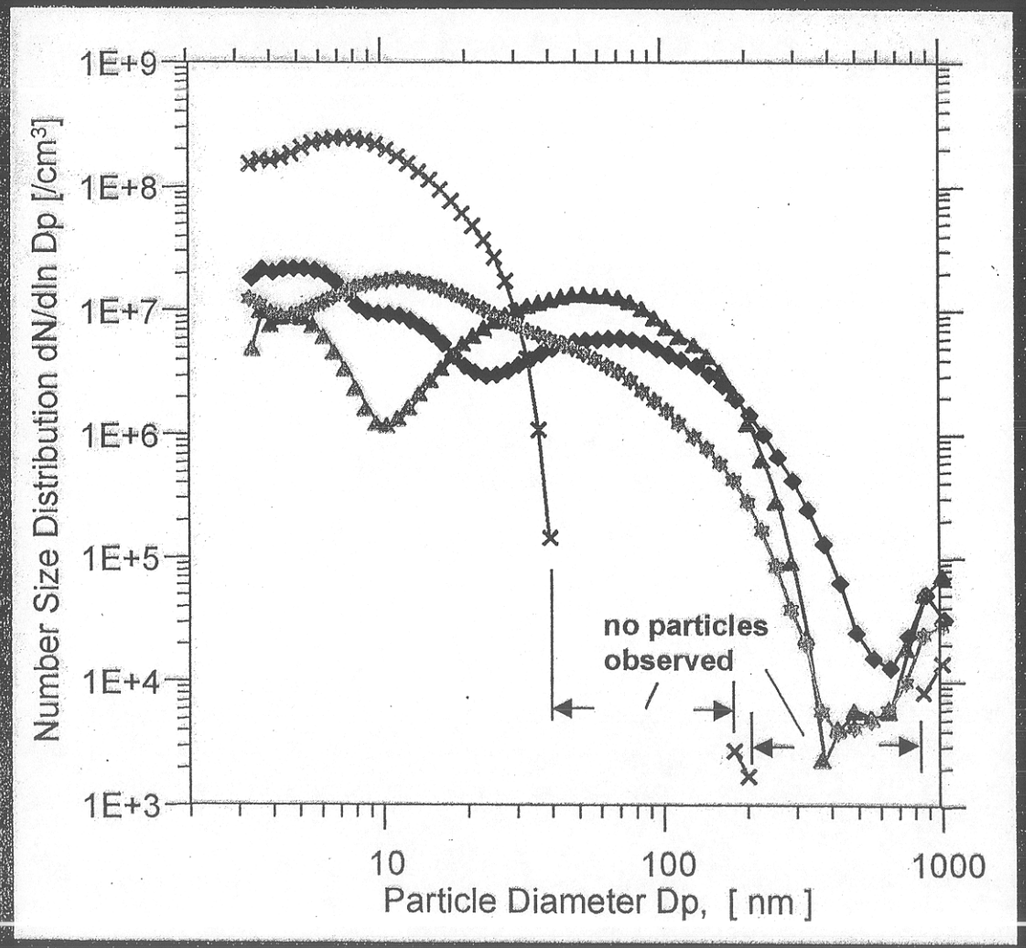



| | | |
|---|---|---|
| **TTM** | **Comp. of Filtration Systems**<br>**(acc. to Zievers et al. / Ceramic Bulletin 1 / 1991)** | **Fig. 32** |

# PM size distribution

TOPTEC "Advancements In Clean Diesel Engine Technology"

## ENGINE COMPARISON in ESC / ECE Tests (Weighted Average)




Low Sulphur Fuel (< 10 ppm) in all cases

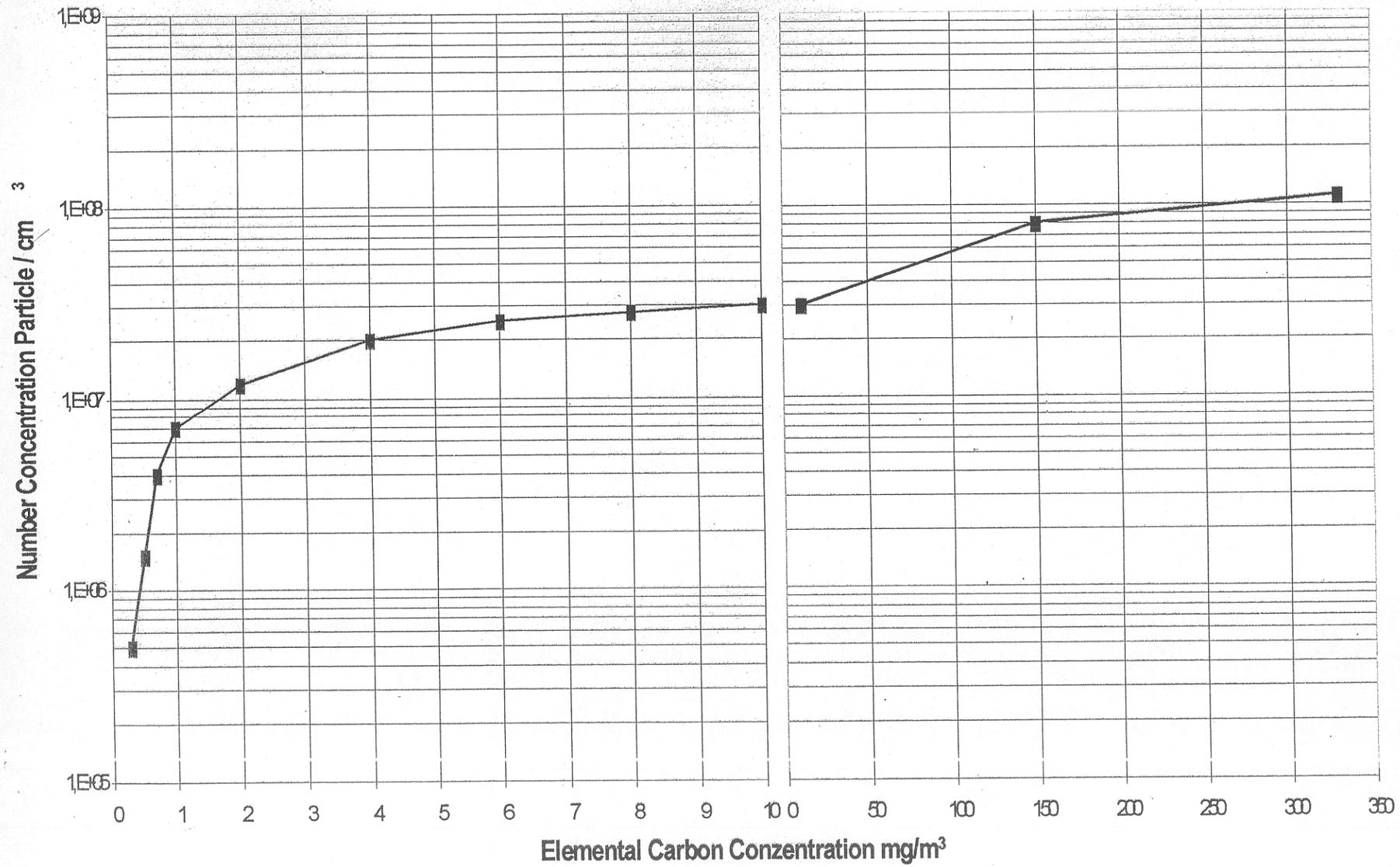
- Euro II in ECE (NOx/PM=6.6/0.11 g/kWh)
- Euro III-EGR in ESC (NOx/PM=4.3/0.074 g/kWh)
- Euro IV-EGR+Trap in ESC (NOx/PM= 2.5/0.017 g/kWh)
- "Euro V" engine-out in ESC (NOx/PM= 9.5/0.025 g/kWh)

**Similar PM size distribution with EURO II, EURO III and "EURO V" engines**

**Increase of nanoparticles on EURO IV engine due to sulphate formation**

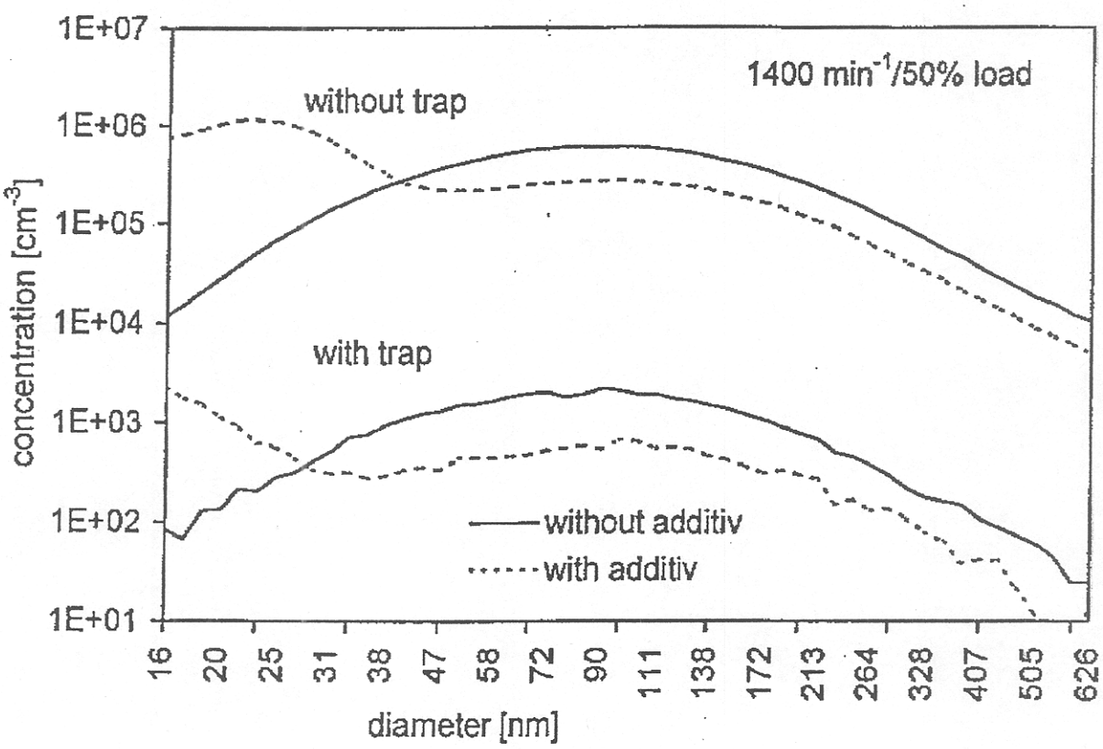
# DEUTZ BF 6 M 2013C - EURO 4

## Particulate Emission - Comparison Number - Mass



# Where are the Additive Oxides left?

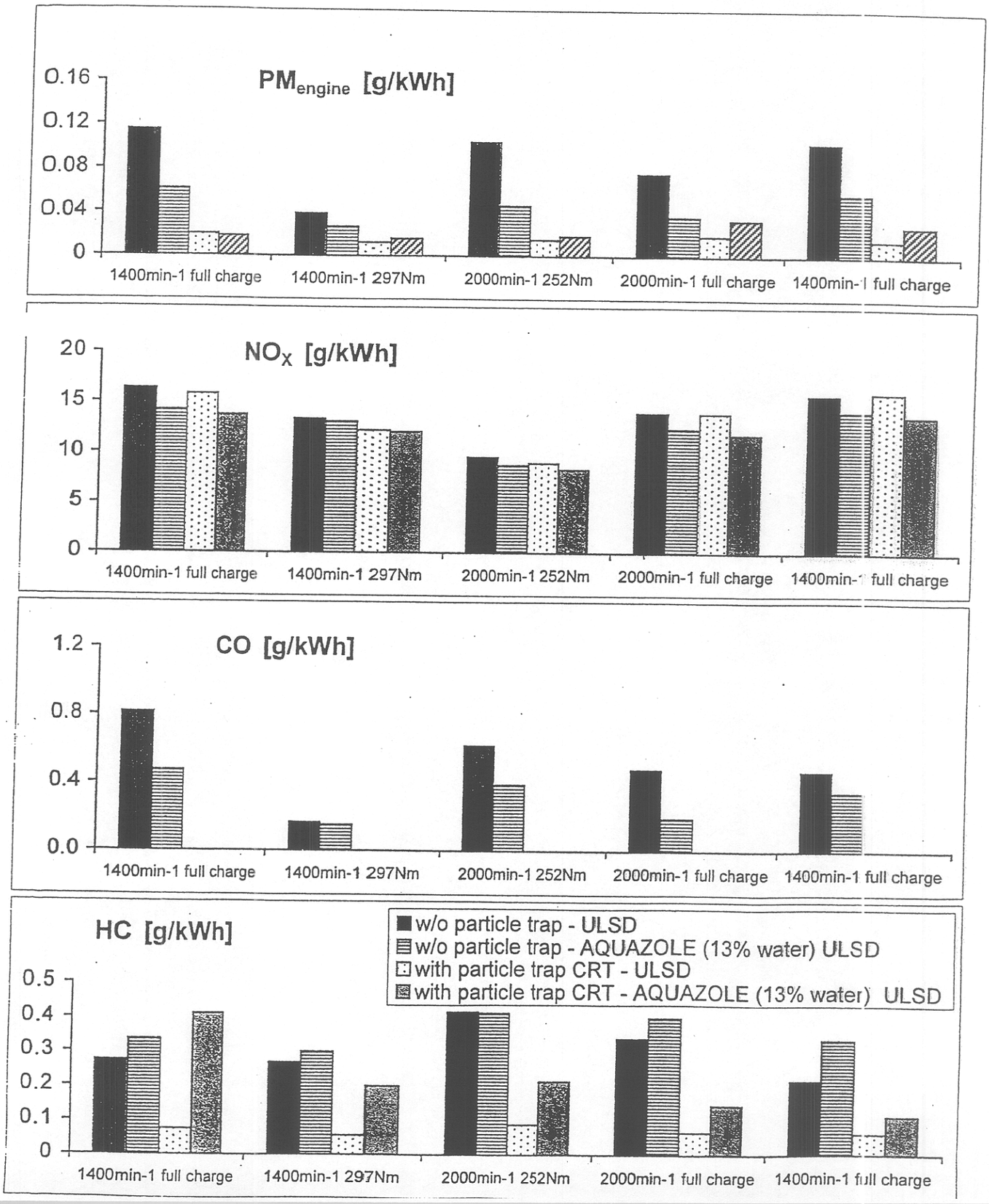
- Some coat the engine surfaces (catalytic activity) mainly in the initial phase
- Some end up in the lube oil (effects unknown)
- Some leave the engine attached to soot particles
- Some leave the engine as small oxide clusters




VERT-data with transition metal additives
Concentration: 100 ppm Ce

# comparison of emissions

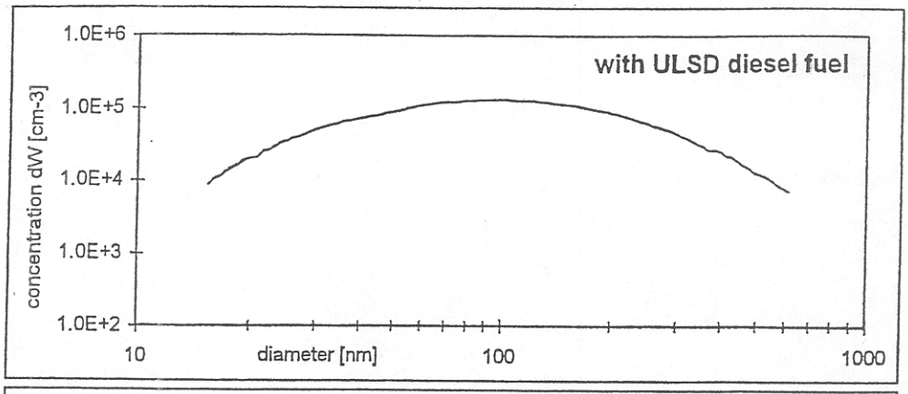
## with / without CRT & AQUAZOLE

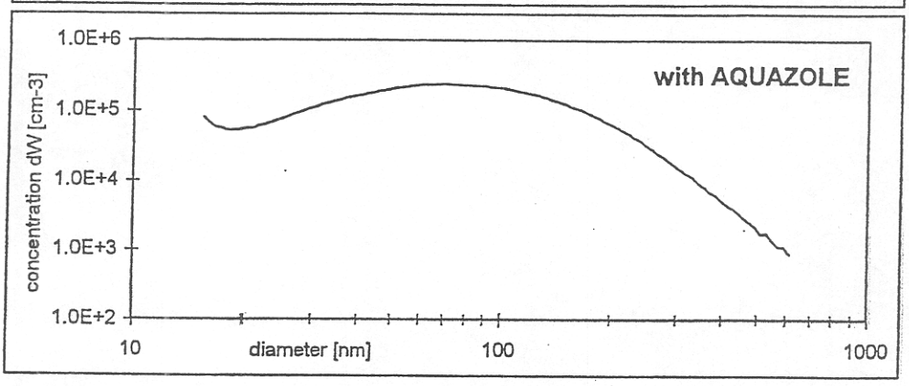


# Size distributions with ELF Fuel, Engine: Liebherr D914T

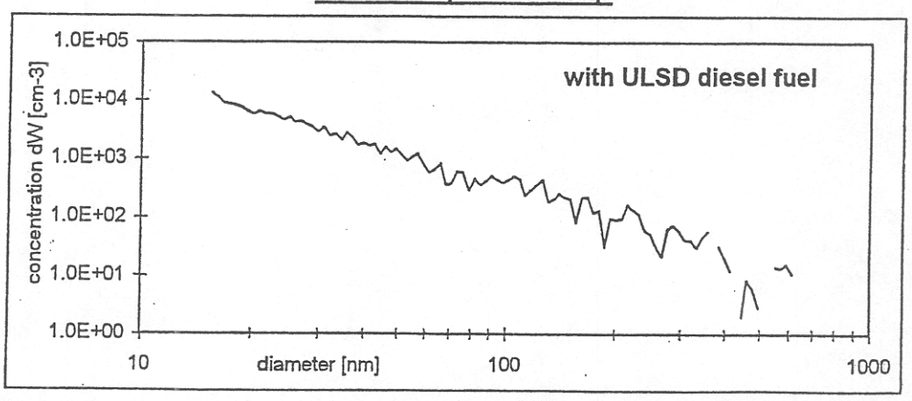
## 1400min$^{-1}$ / full load - mean of 3 samples, with thermodesorber

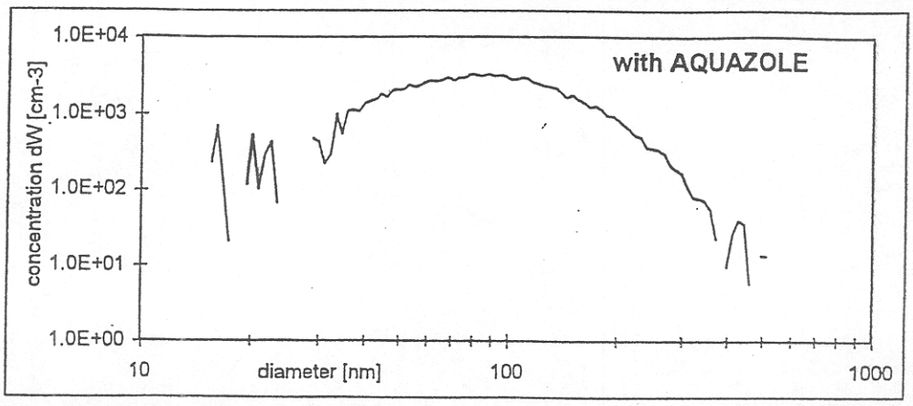
### without particle trap




### with CRT particle trap

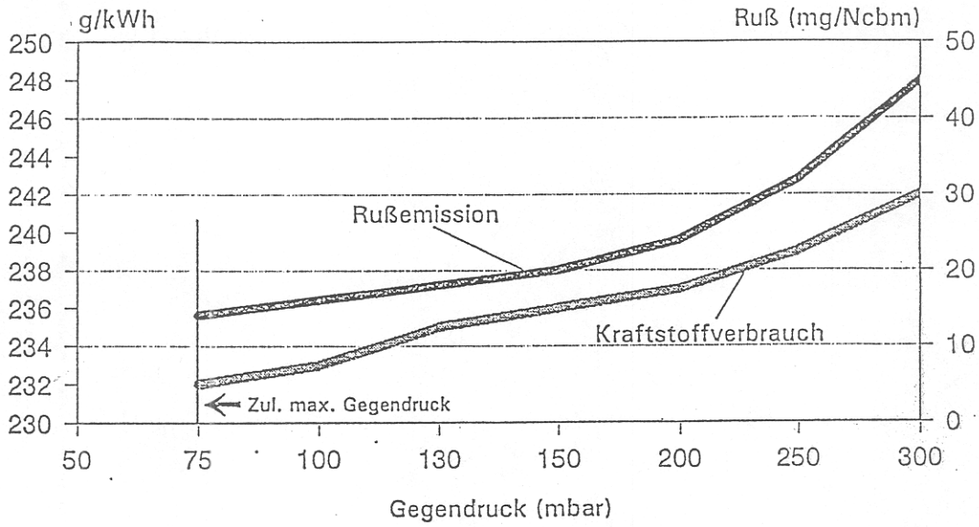



O20606.xls

# Negative Effekte von Partikelfiltersystemen

- Druckverlust: im Fahrzeug 100 - 200 mbar
  (bei Stationärmotoren wird < 20 mbar verlangt)
  - Bisheriger Grenzwert für Schalldämpfer + Kat: < ca. 60 - 80 mbar
  - ab ca. 300 mbar steigen Emissionen, Bauteiltemperaturen und Brennstoffverbrauch überproportional an.




**Zum Vergleich:**

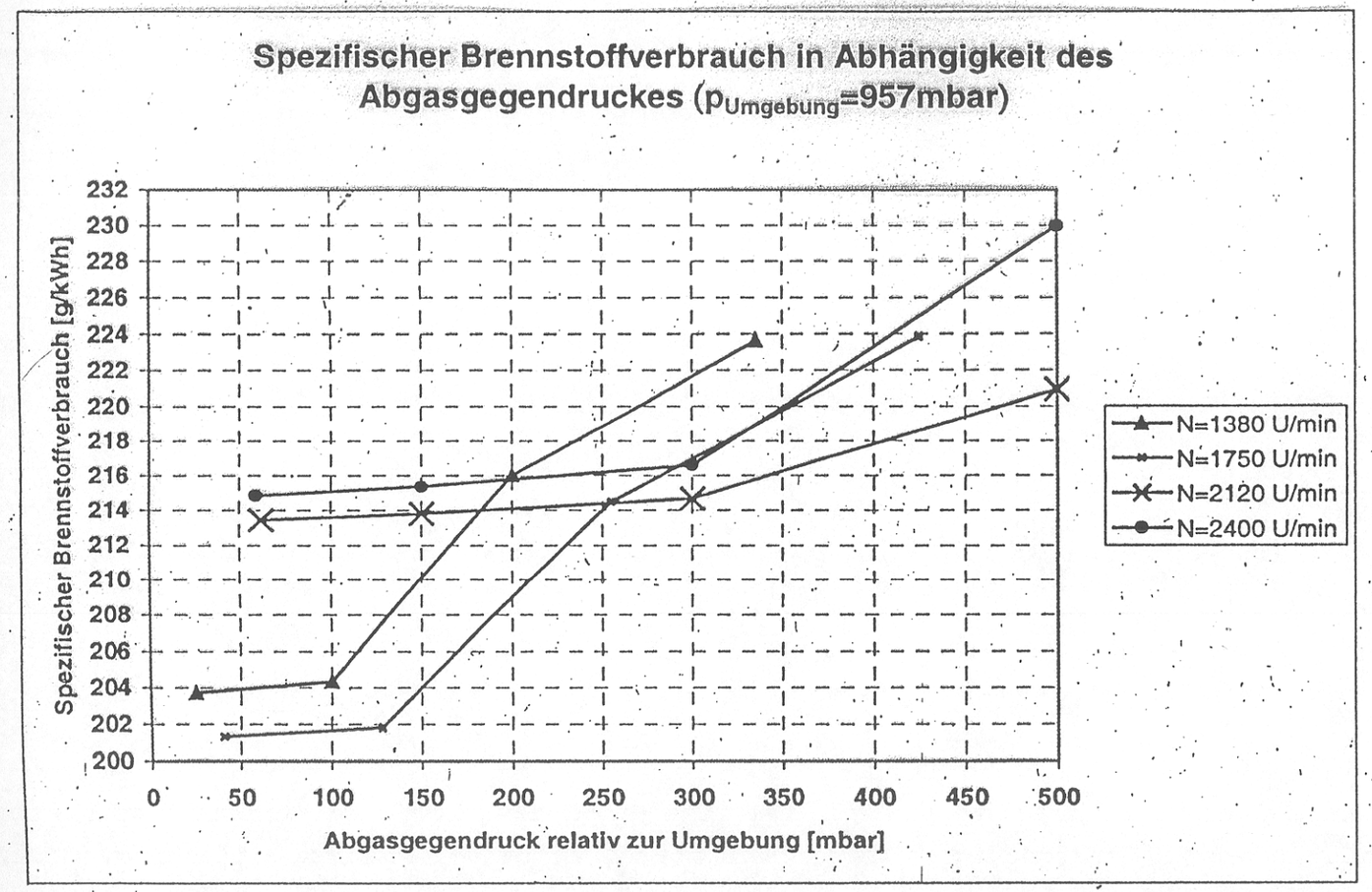
| | |
|---|---|
| - Motormitteldruck: | 10 - 20 bar |
| - Motorspitzendruck: | 140 bar |
| - Motorbremsengegendruck: | ca. 10 bar |

- Erhöhung Brennstoffverbrauch

  Grundsätzlich gemäss $\frac{\delta B_e}{B_e} = \frac{\text{Druckverlust}}{\text{indizierter Mitteldruck}}$

  Beim Nutzfahrzeug-Motor ist eine Verschlechterung des Brennstoffverbrauchs um 3 - 6 % zu erwarten

- Aktive Systeme wie Brenner und elektrische Beheizung brauchen Zusatzenergie. Beim Brenner unter 1%,
  Elektroheizung ca. 2 - 3 % der Nutzleistung (?)




Figur 52: Verschlech-ter
des Brennstoffverbrauch
4 Volllastdrehzahlen info
Steigerung des Abgasge
gendruckes.

Die vergößerte Darstellung von Bild 8 in Bild 9 demonstriert nochmals eindeutig den Effekt der Eisenablagerungen in den Kanälen und die örtliche Schmelzwirkung im Filter. Bei Betrachtung der unteren Kanäle werden ebenfalls die Pinholes mit geschwärzten (festverbackendem - Magnetit) Rand sichtbar

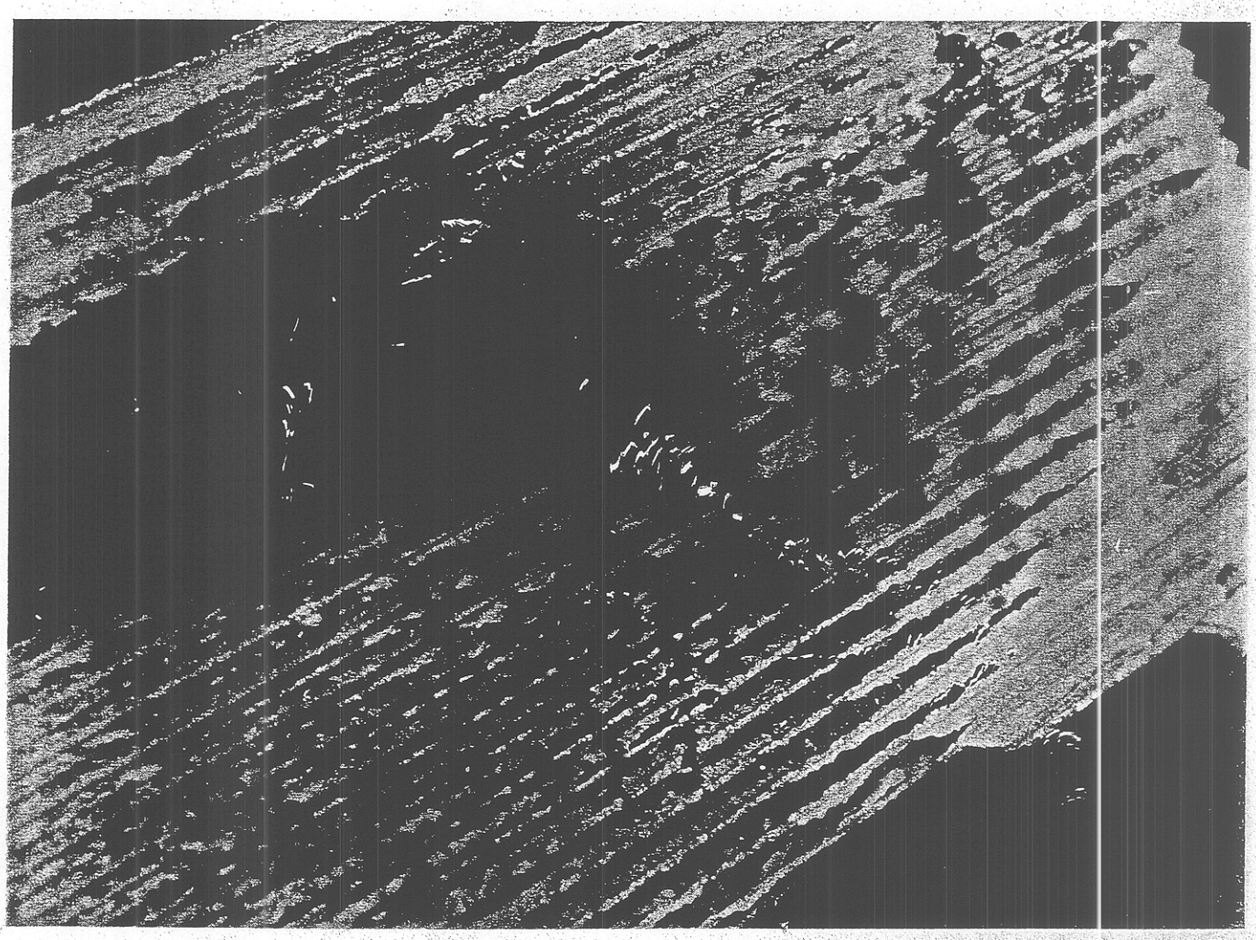
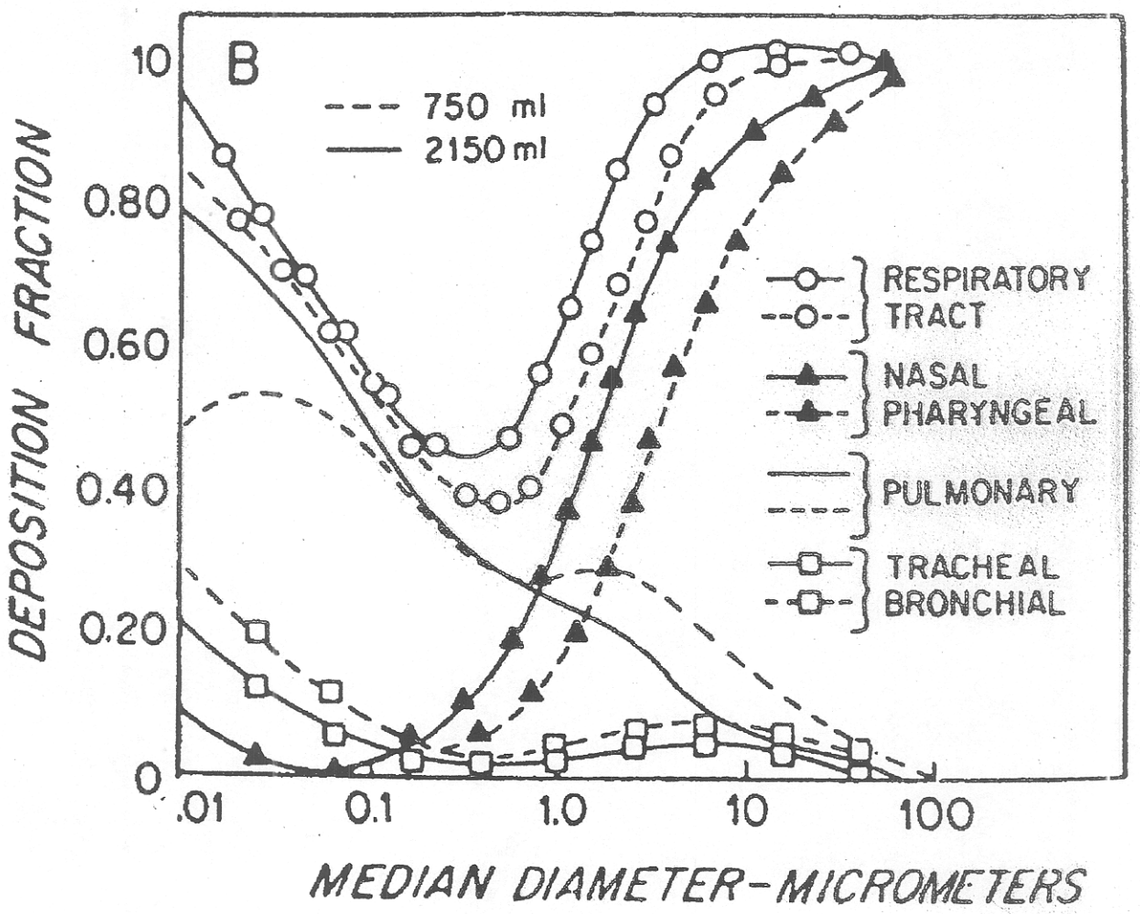


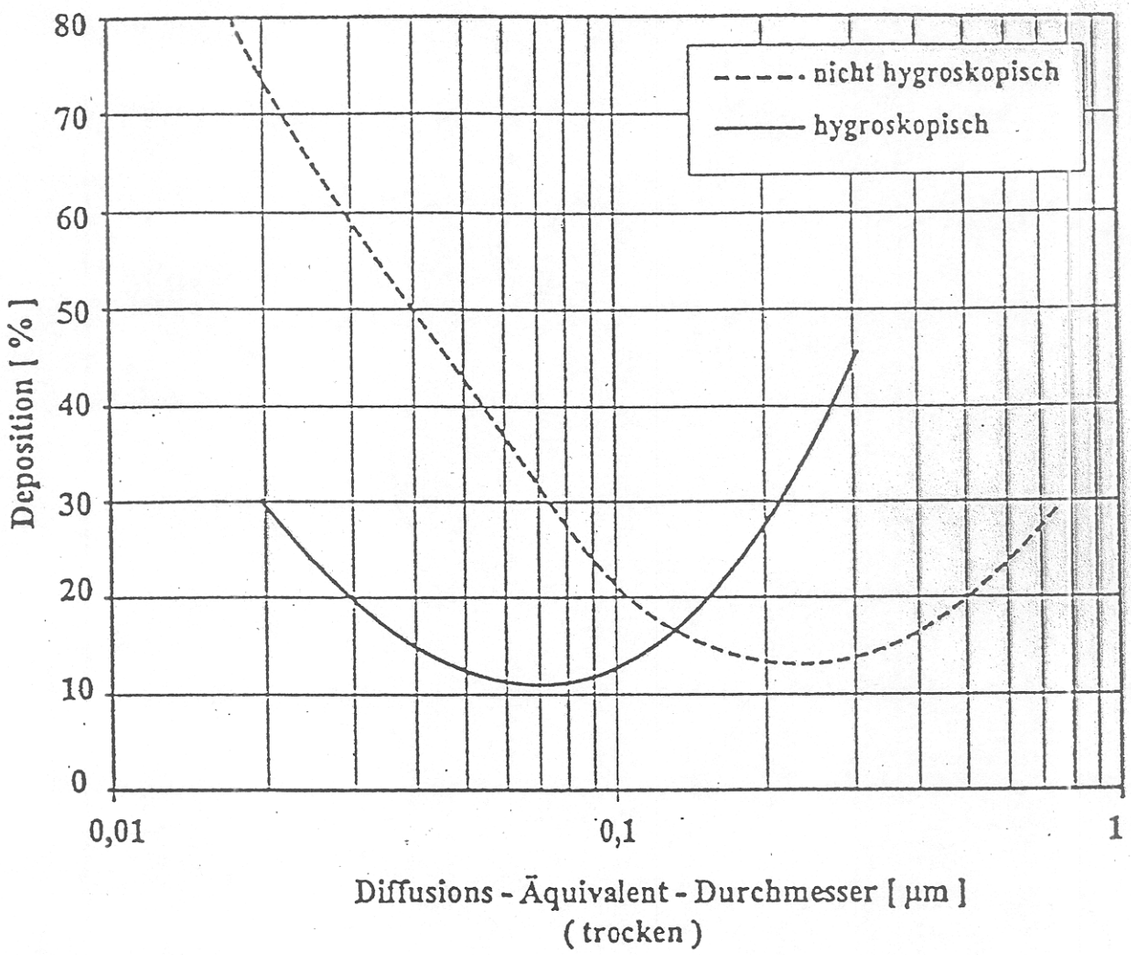
Bild 9: Vergrößerung von Bild 8 mit Schmelzkavernen, Fe-Ablagerungen und Pinholes.

# Abscheidung von Feinpartikeln in Nase, Bronchien und Alveolen



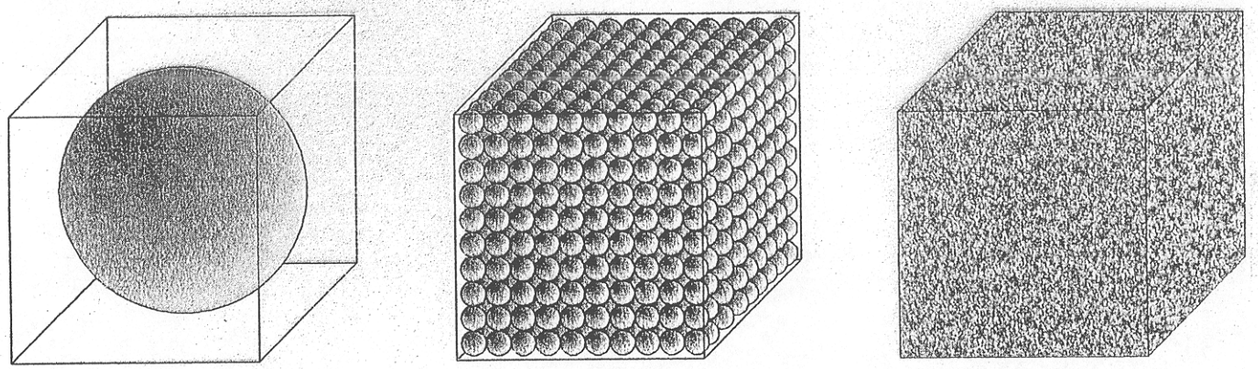

Quelle: Hinds, Aerosoltechnologie, 1982

# Depositionswahrscheinlichkeit von Feinstpartikeln im Alveolarbereich



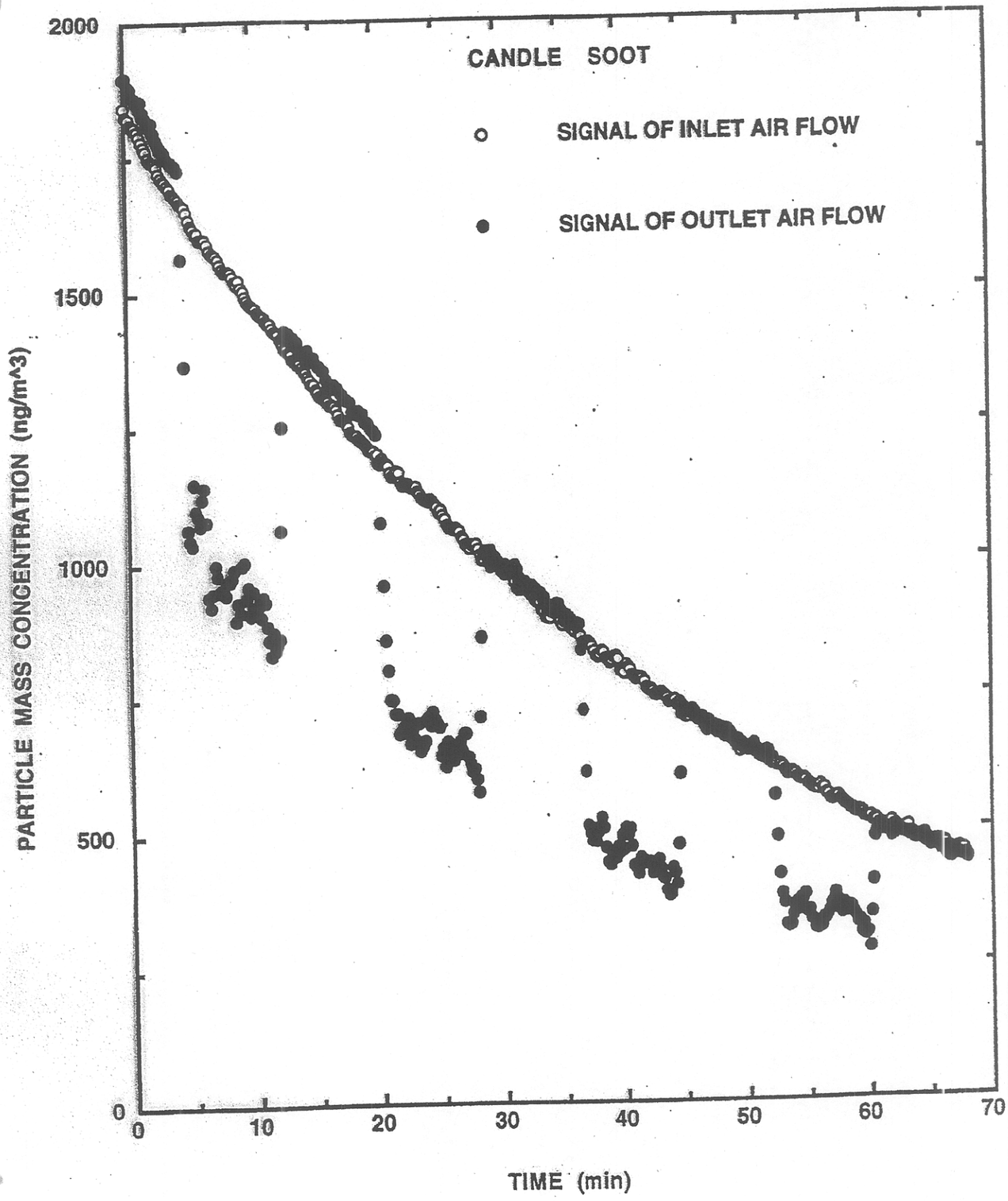

Quelle: MAK: Aerosole-Stäube-Rauche und Nebel, 24. Lieferung 97

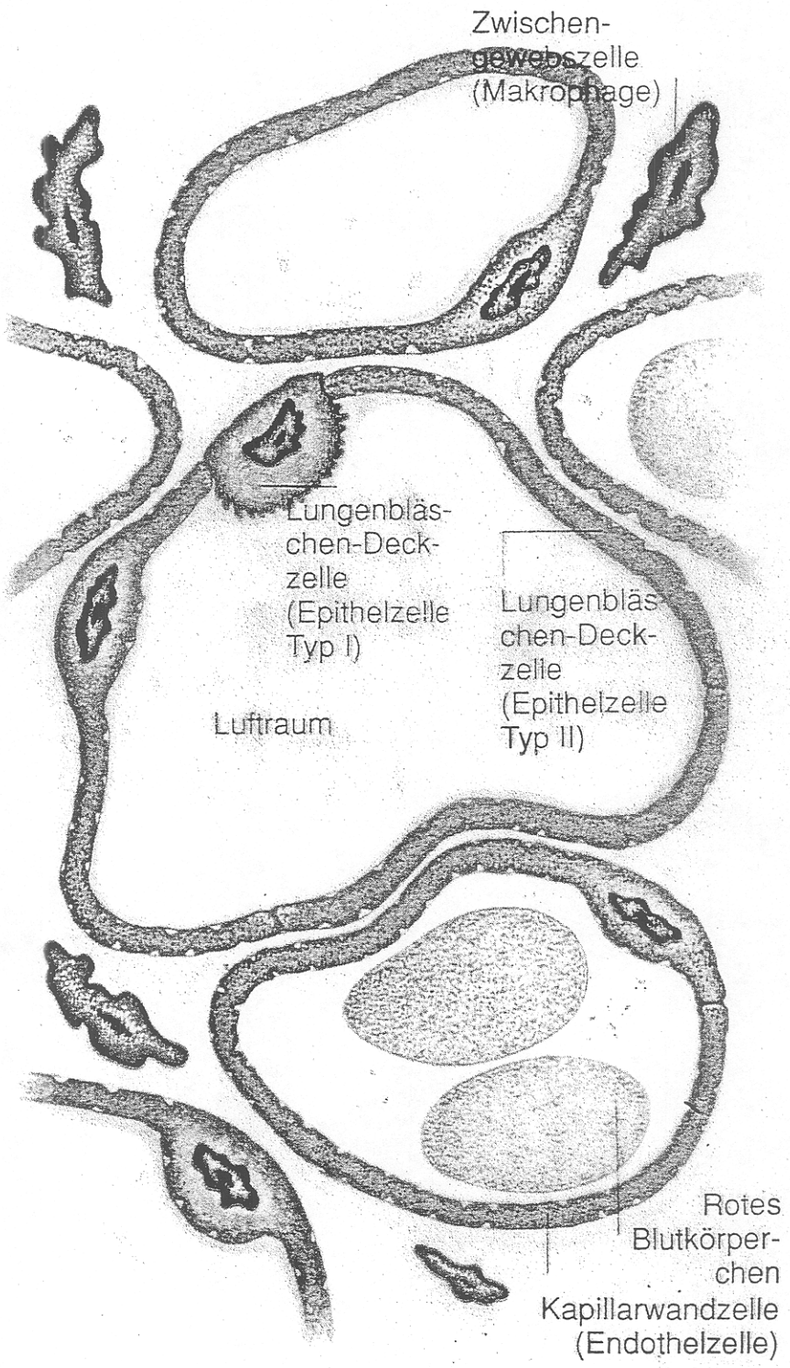
# Zusammenhang Partikelzahl und Oberfläche



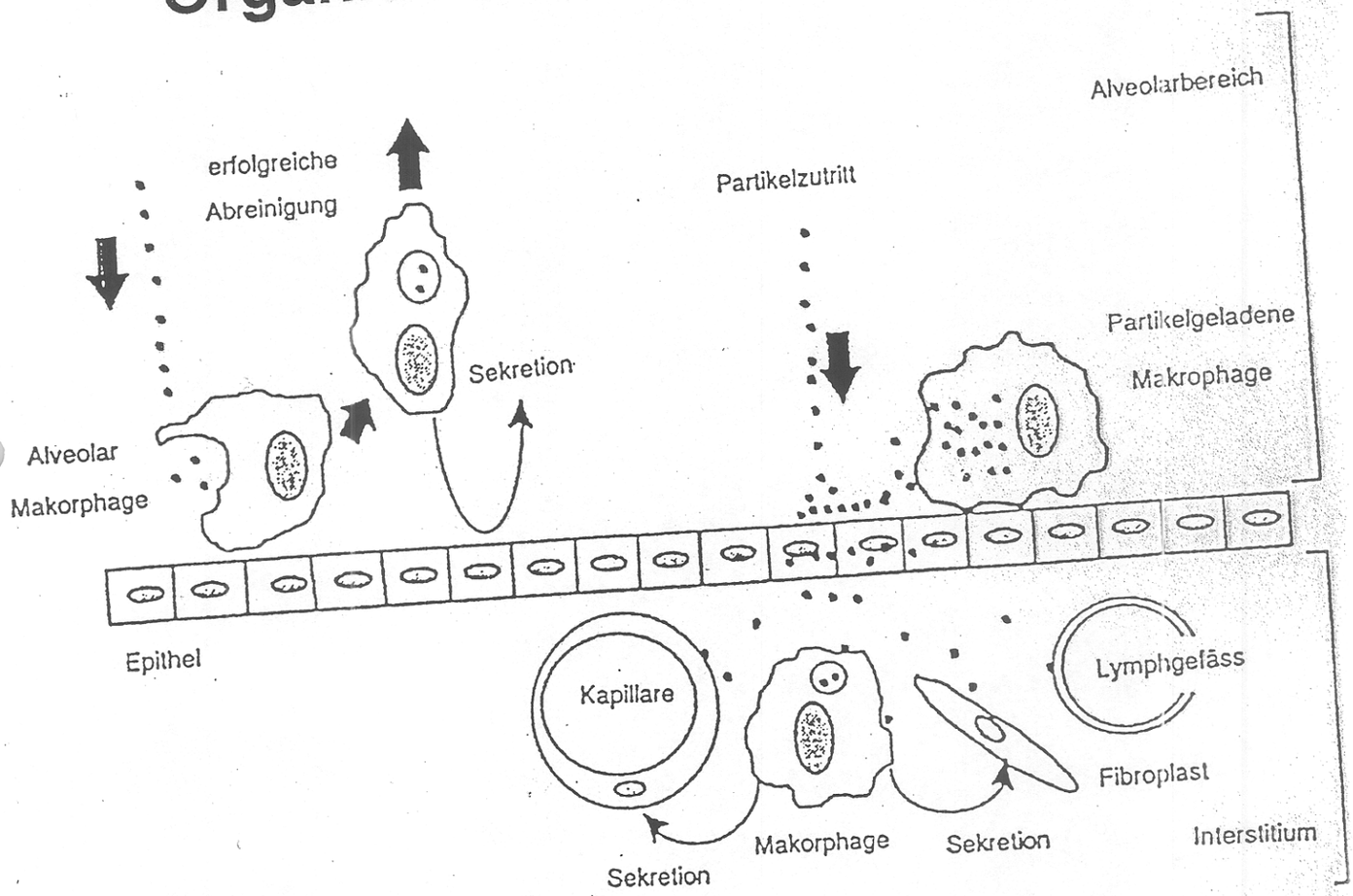
| Partikeldurchmesser | 1µm | 0,1µm | 0,01µm |
|---|---|---|---|
| Partikelzahl | 1 | 1000 | 1000000 |
| rel. Gesamtoberfläche | 1 | 10 | 100 |
| relative Masse | 1 | 1 | 1 |
| rel. Oberfl. des Partikels | 1 | 0,01 | 0,0001 |
| Volumen der Partikel | 0,5 µm³ | 0,5 µm³ | 0,5 µm³ |
| Vol. des einz. Partikels | 0,5 µm³ | 0,0005 µm³ | 0,0000005 µm³ |

# SOOT DEPOSITION IN THE HUMAN RESPIRATORY TRACT



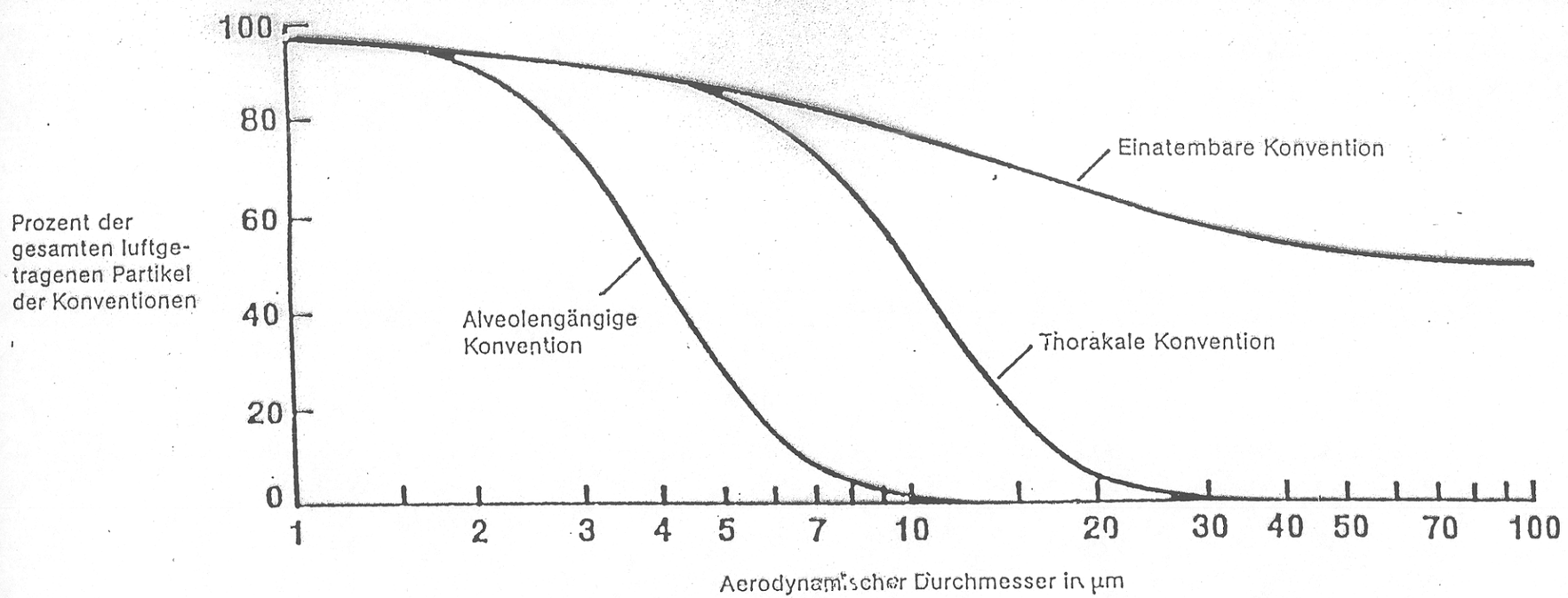

Zwischen-
gewebszelle
(Makrophage)
Lungenbläs-
chen-Deck-
zelle
(Epithelzelle
Typ I)
Lungenbläs-
chen-Deck-
zelle
(Epithelzelle
Typ II)
Luftraum
Rotes
Blutkörper-
chen
Kapillarwandzelle
(Endothelzelle)

# Der Weg der Partikel in den Organismus

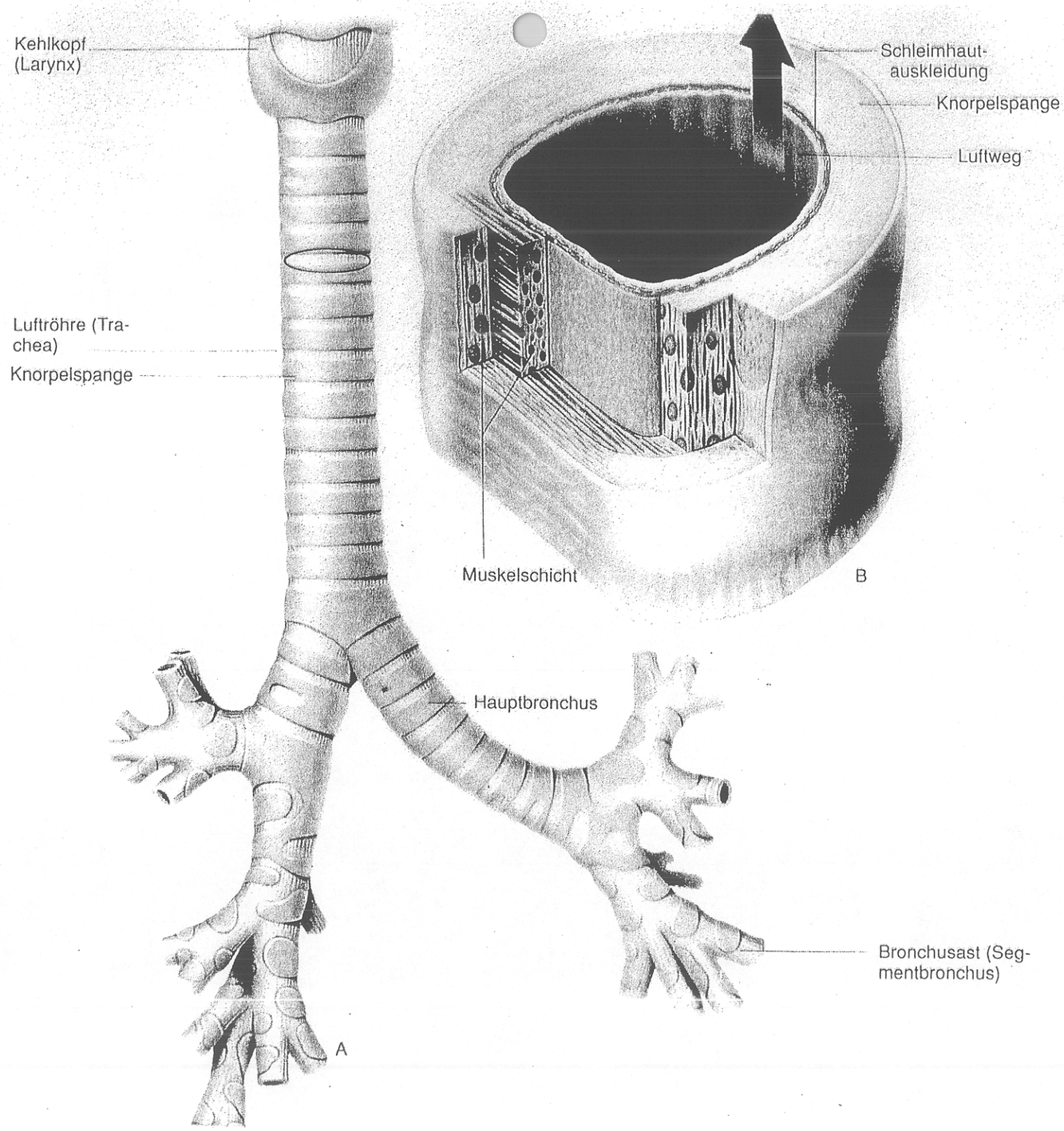



Quelle: Ultrafine (Nanometre) Particle Mediated Lung Injury
Donaldson et al., J.Aerosol Sc. 5.6 1998

# Aerosol-Conventions according to EN 481




Die einatembare, thorakale und alveolengängige Konvention in Prozent der gesamten luftgetragenen Partikel


Kehlkopf (Larynx)
Luftröhre (Trachea)
Knorpelspange
Schleimhautauskleidung
Knorpelspange
Luftweg
Muskelschicht
B
Hauptbronchus
Bronchusast (Segmentbronchus)
A

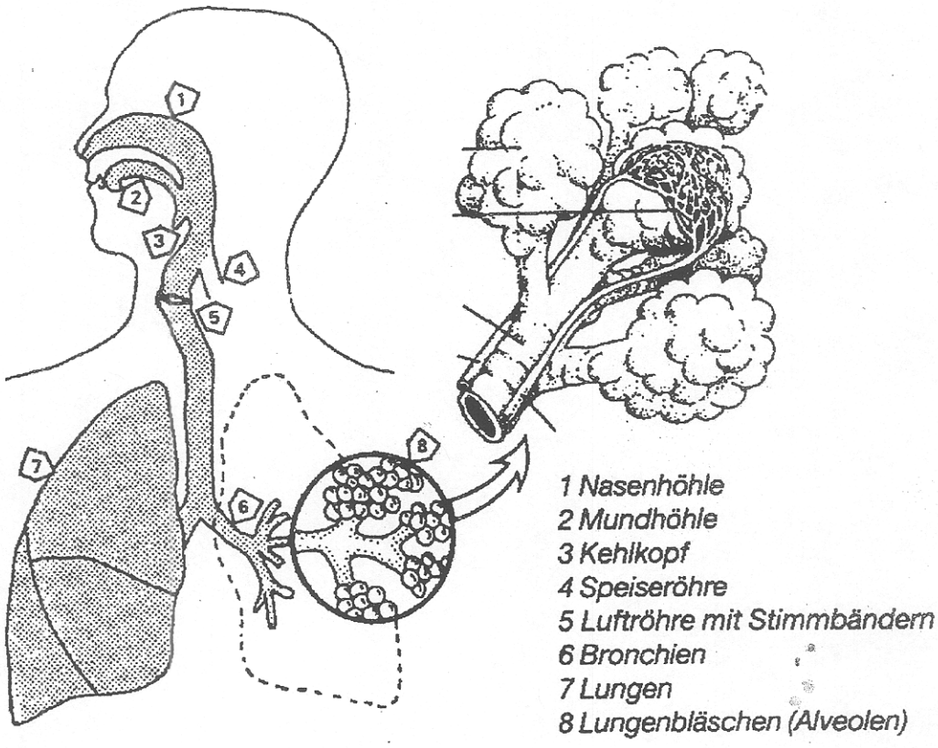
$$B = \frac{D}{kT} = \frac{C}{3\pi\,\eta\,d} \sim \frac{1}{d^2}$$

B = Beweglichkeit des Teilchens
D = Diffusionskoeffizient des Teilchens
k = Boltzmann-Konstante
T = absolute Temperatur
C = Gleitkorrekturfaktor des Teilchens (Cunningham-Korrektur)
C nähert sich für kleine Partikel < 100 nm einer 1/d-Abhängigkeit
$\eta$ = Zähigkeit des Dispersionsmittels (hier: Luft)
d = Teilchendurchmesser

Quelle: Ultrafeine (Aerosol)-Teilchen und deren Agglomerate und Aggregate
Messung von Gefahrstoffen, 21. Lfg. X/98, BIA Arbeitsmappe 0412/5

# Die Lunge

## Einfallstor für Luftschadstoffe




- 23 m3 Luft pro Tag
- 5-20 l Luft pro Minute / 5-10 l Blut pro Minute
- Austauschfläche 30-100 m2
- 500'000'000 Alveolen ( 5000'000'000 Partikel pro l Abgas)
- 2000 km Kapillaren
- 23 Verzweigungen von Nase bis Alveolen
- Geschwindigkeitsverminderung 1:250
- Restgeschwindigkeit in den Alveolarkanälen: 0,1 cm/s
- Verweilzeit 1 s
- Gasaustausch durch 2 Zellschichten ca 1 $\mu$m

Quelle: Birgersson, Chemie und Gesundheit