Morphological characteristics of diesel emission particles from image analysis of electron microscopy images

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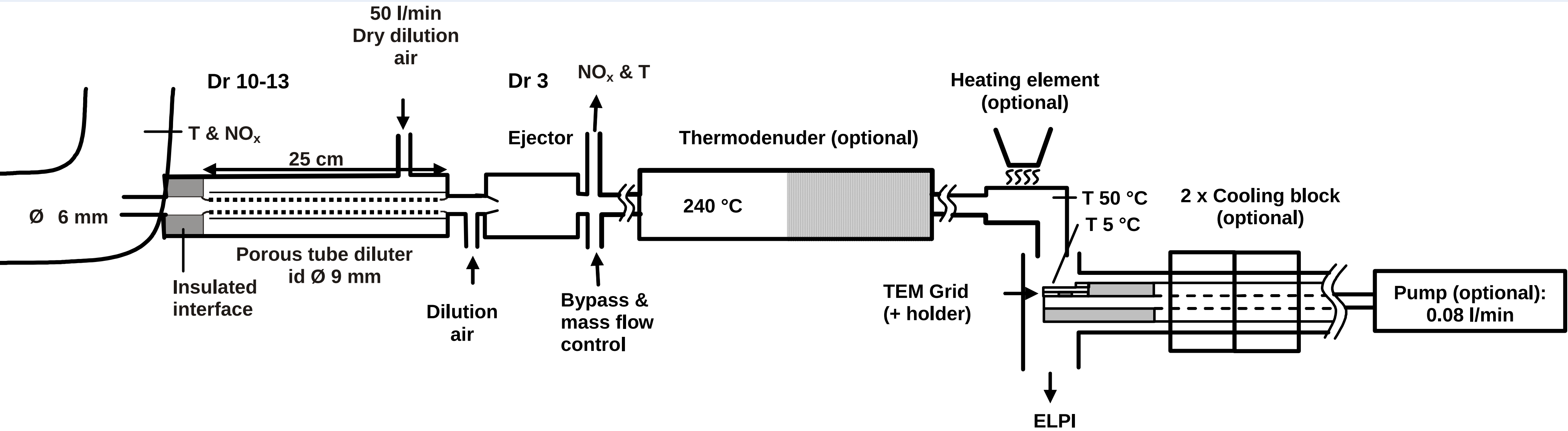
Objectives

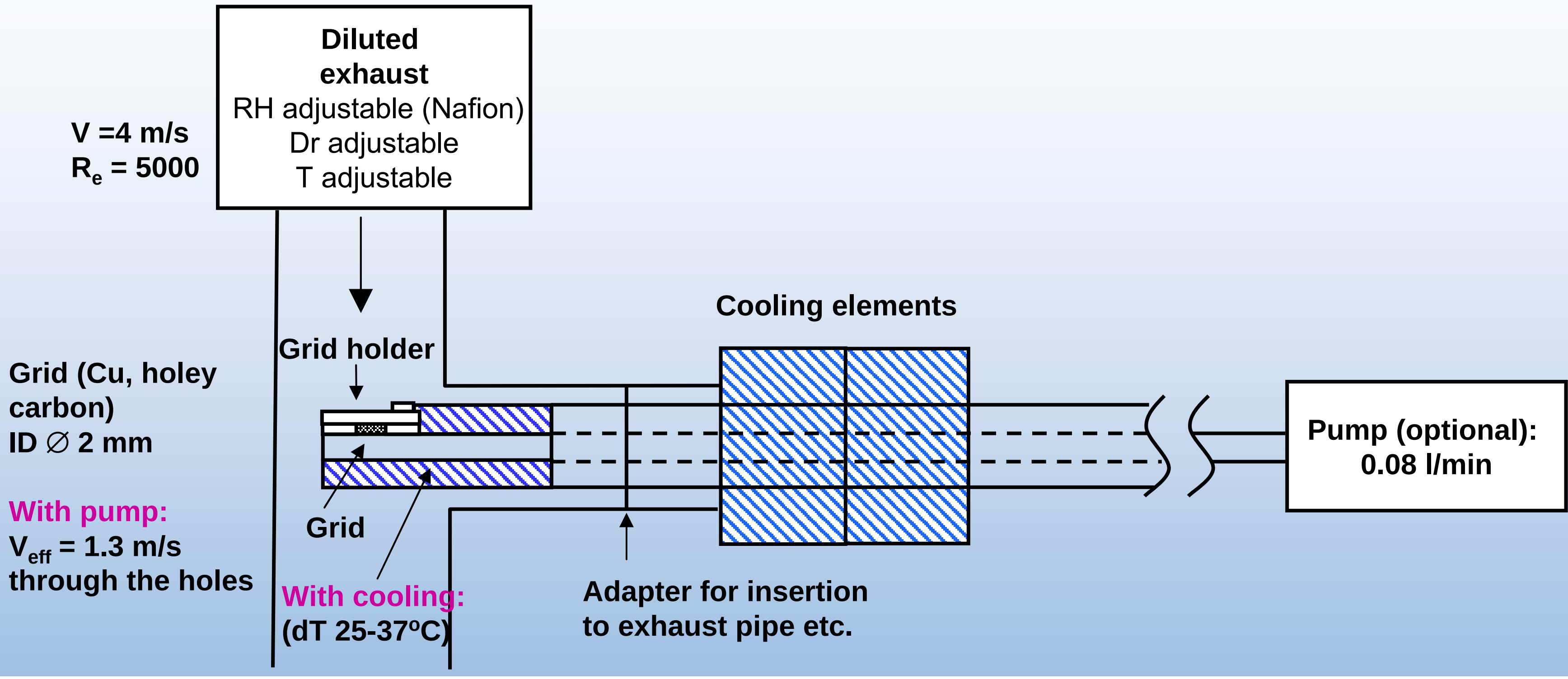
- To develop a simple, non-discriminating sampling system for diesel particle emission for EM imaging and analysis
- To analyse representative, native particle populations

  To study morphological properties of diesel particles from 2D projections of EM images
- To develop a method for *semi-automatic* analysis of size, shape and fractal properties of diesel particle aggregates
- To develop a method for *semi-automatic* analysis of primary particle size distribution in diesel agglomerates
- To study particle structures containing volatile matter

Sampling system for SEM/TEM specimens

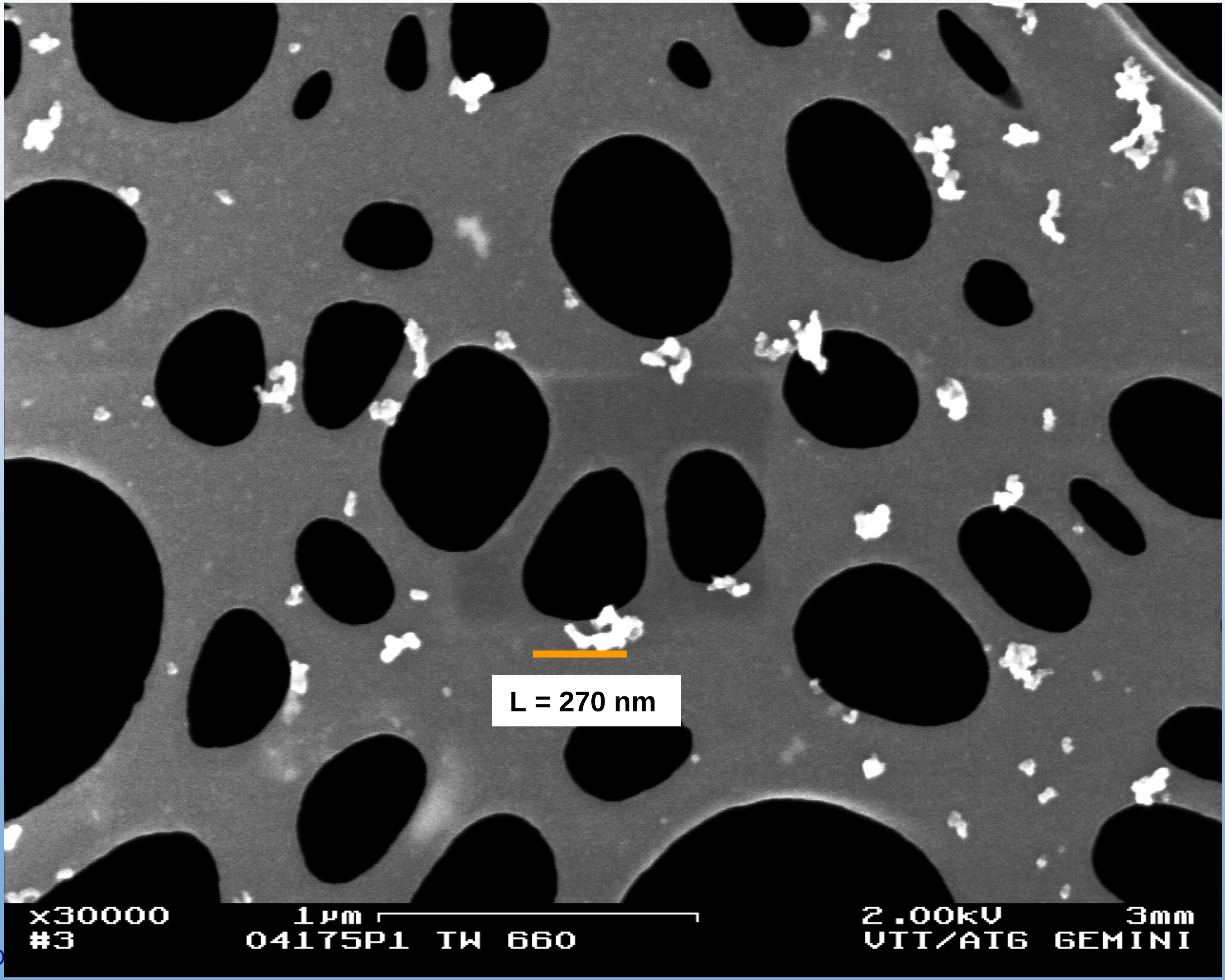


Sampling head for electron microscopy sampling

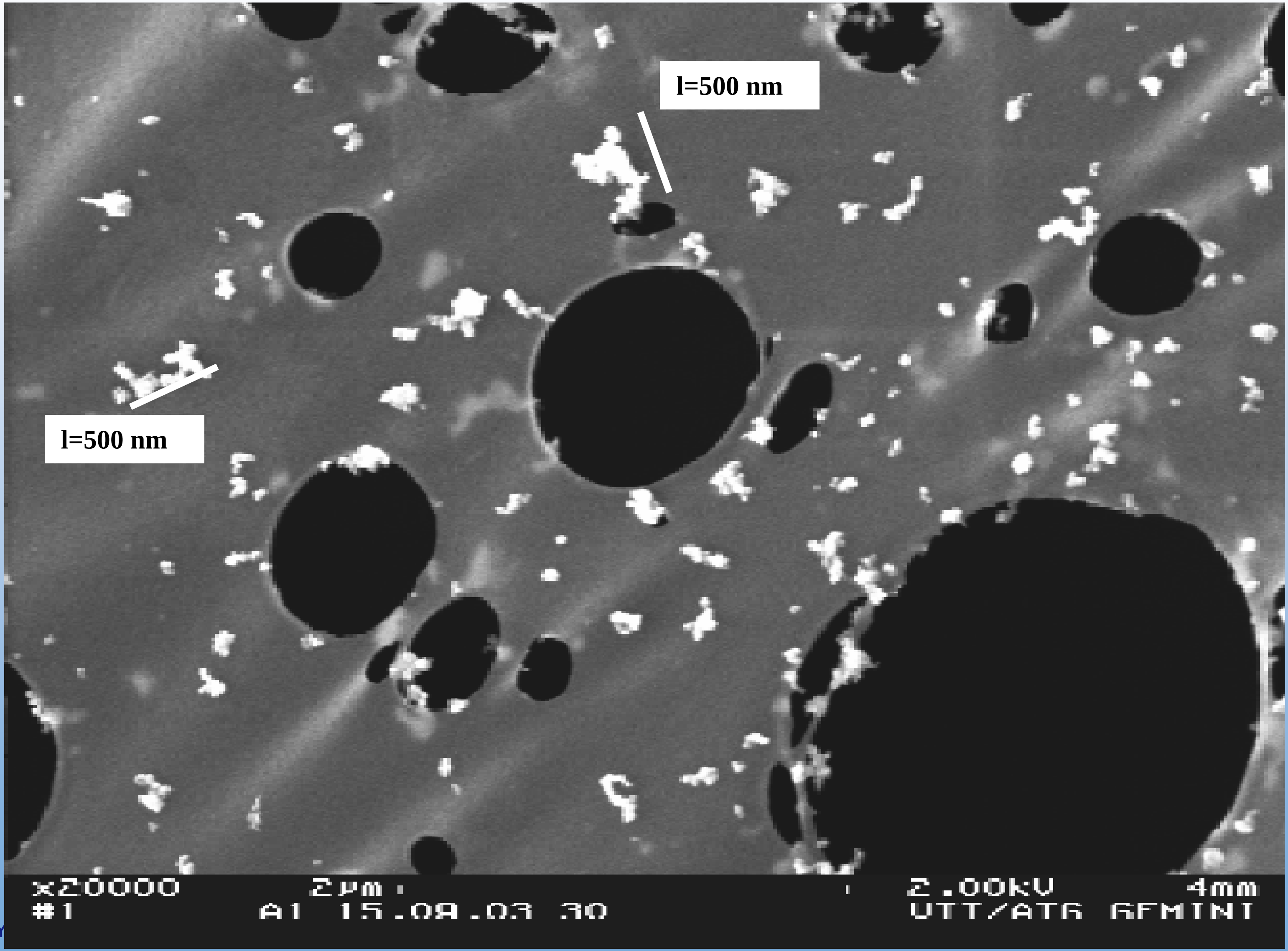


- Target: non-size selective, non-artefact forming sampling system with moderate sampling times
- Sampling time range for thermophoresis 10 – 120 min with dT 25 – 37 °C
- Shorter times achievable with more efficient warming up of the diluted emission
- Shorter times achievable with more efficient cooling of the grid holder block (providing drying of the emission due to the dew point problems encountered)
- Sampling time range for pump sampling 5 – 90 s
- Thermophoretic and pump sampling were compared

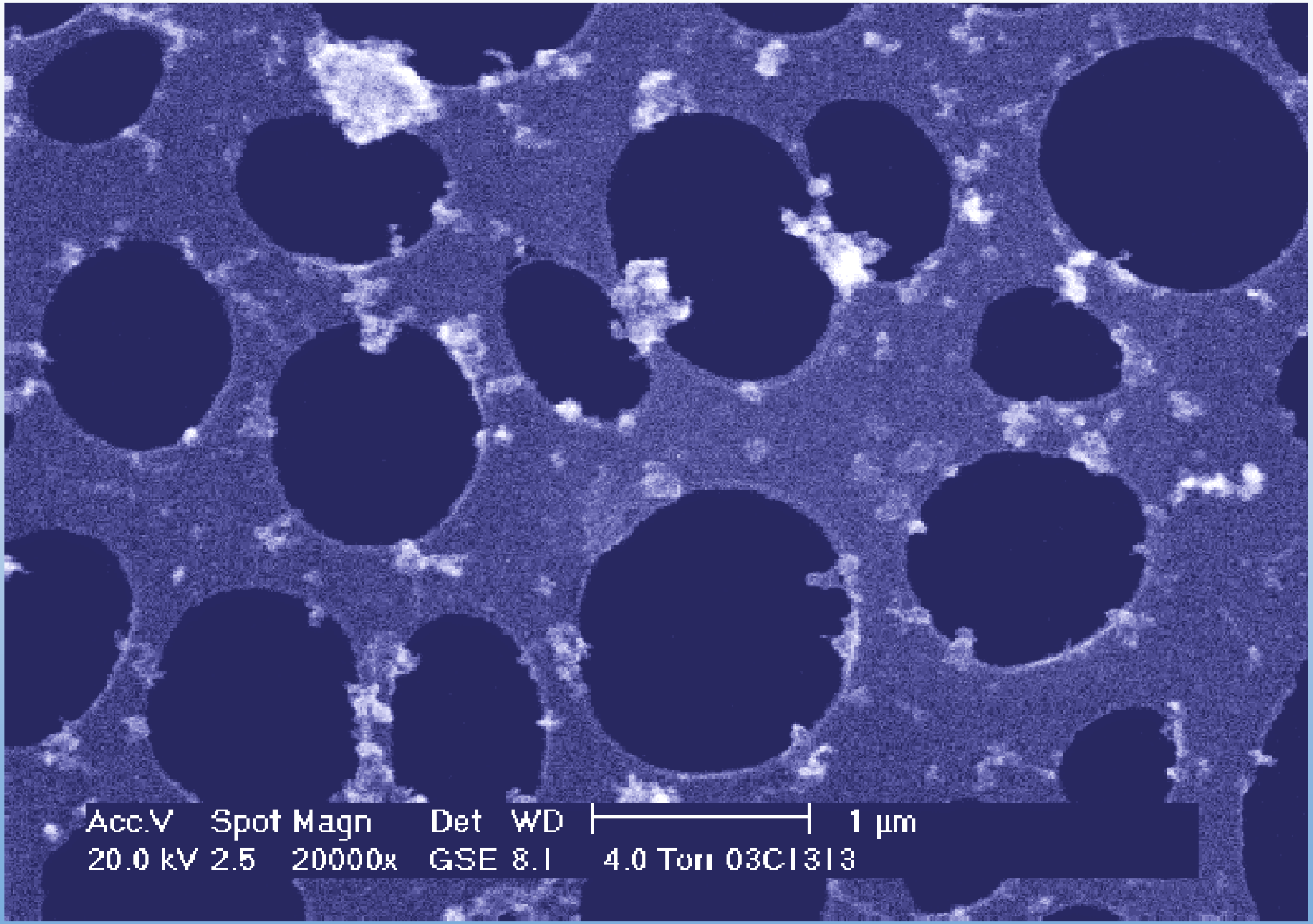
Neat sample density and population for SEM image analysis / Thermophoretic sampling



SEM population sampled with pump (1 – 1.5 m/s)



”Best quality” ESEM image for volatiles study



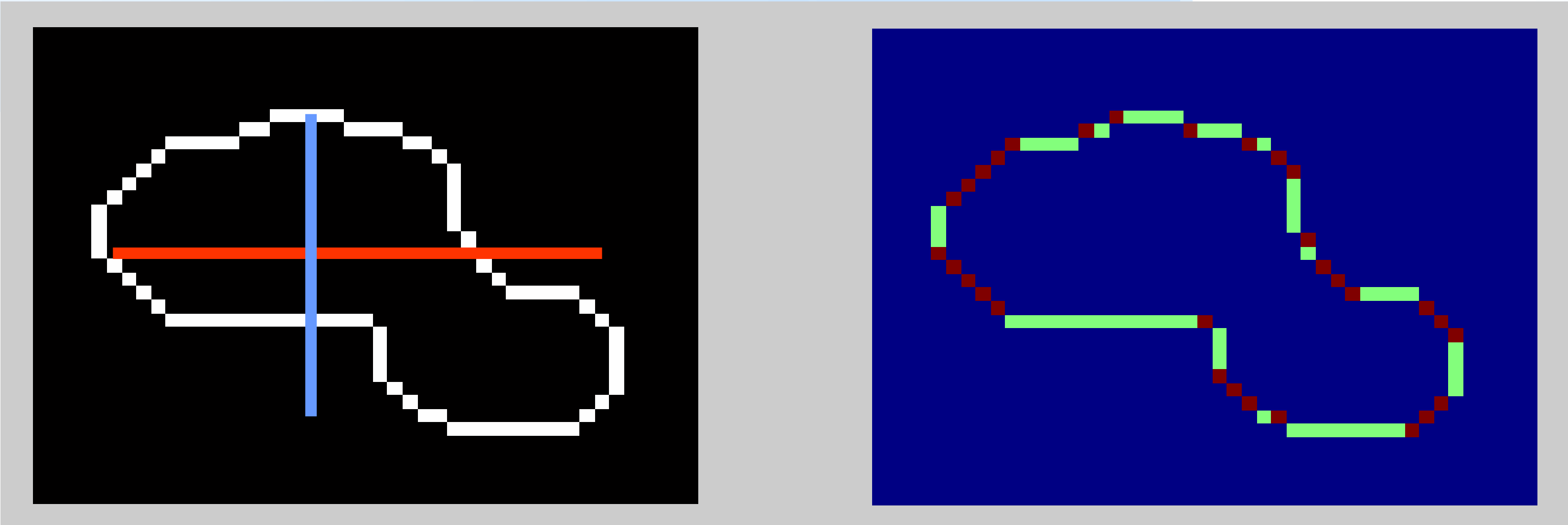
Principles of calculation from SEM images

- To study populations 400 – 1200 particles from x 2-30 000 magnified images analysed (5 to 20 images).
- Calculated are distributions for aggregate perimeter *p*, projected area *A*, equivalent diameter D_{eqv}, maximum length *L* and maximum orthogonal width *W*.

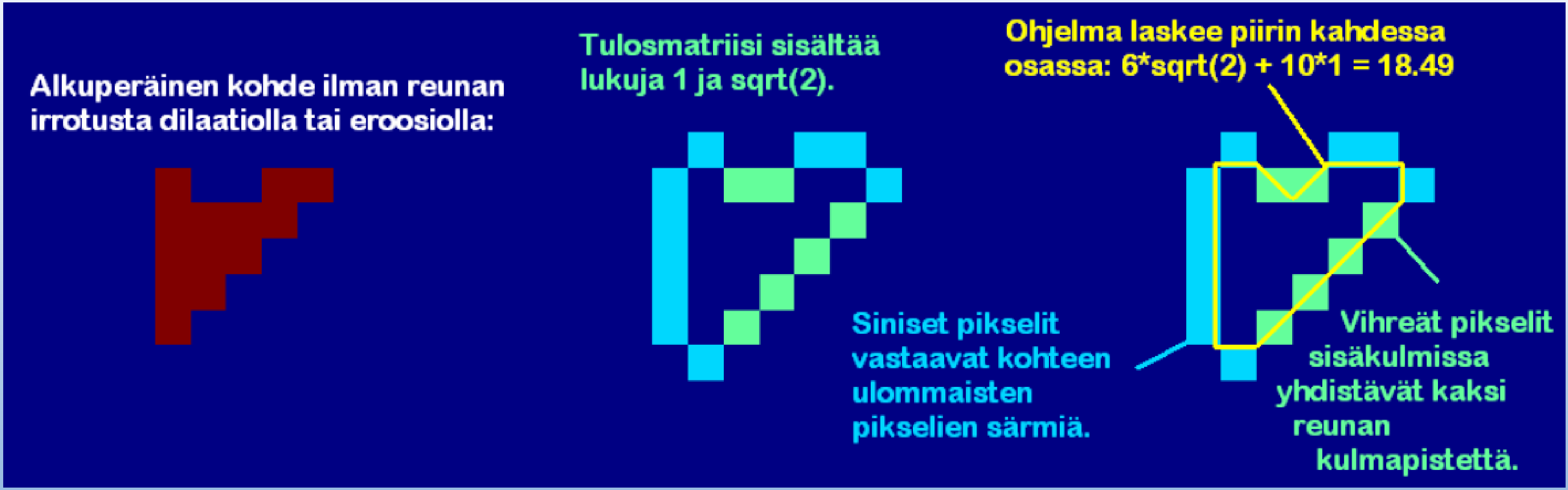
  Contour is set by thresholding the image; based on operator judgement of the edge position.
- Perimeter is calculated by chain code algorithm.
- Perimeter is calculated from the difference of original image and its dilation
- *A* and D_{eqv} are calculated from the number of pixels.
- In automatic analysis the minimum number of pixels for *p, L* and *W* analysis is limited to 9-12 pixels corresponding ~ D_{eqv} 20 nm. Smallest particles are filtered away.
- Manually it is possible to accept particle size down to 1 pixel.

Perimeter is computed by chain code algorithm from original image.

Max length L and max width W are calculated from a magnified image; they are orthogonal distances on the original (thresholded) target area



Principle of perimeter calculation

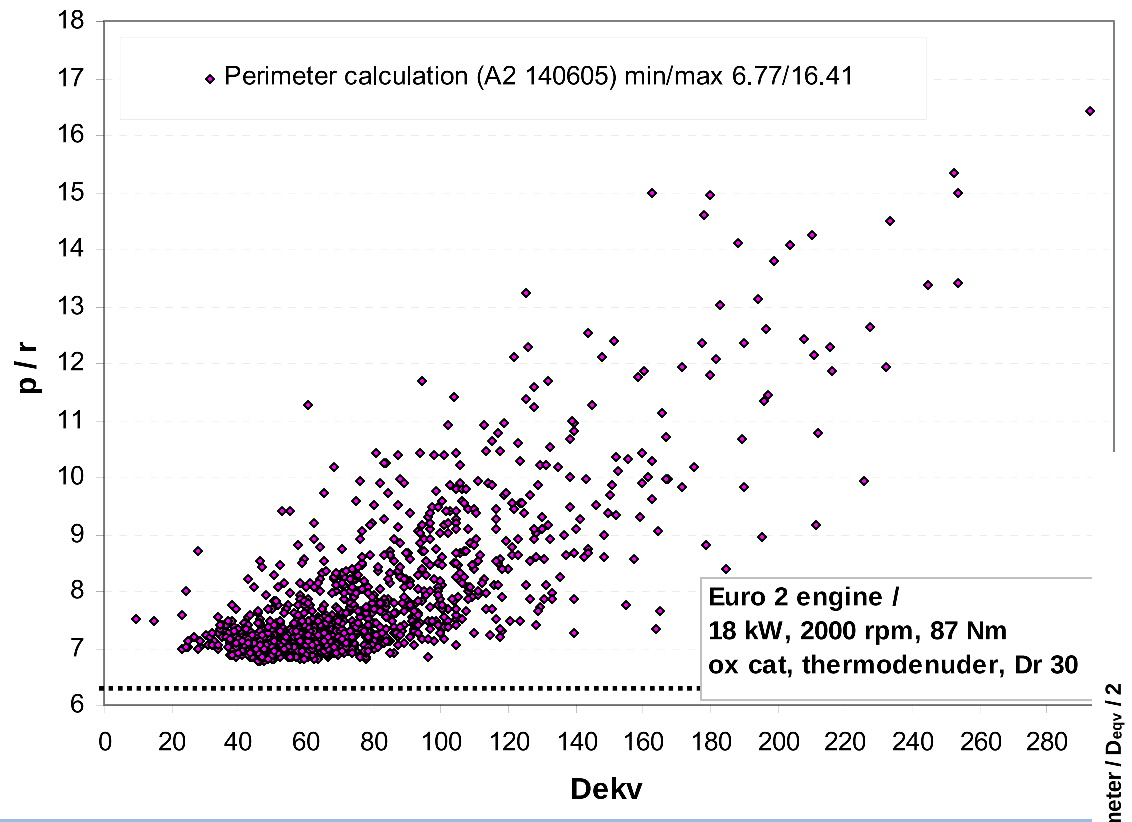


Original object without contour separation by dilation or erosion

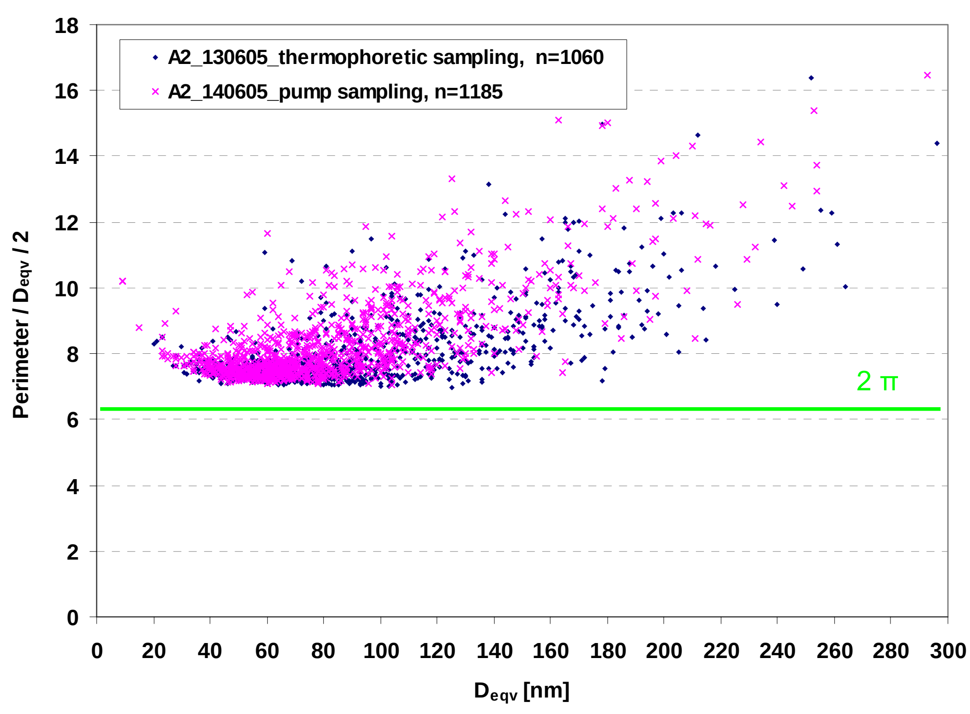
Result matrix contains figures 1 and sqrt(2)

Program calculates perimeter in two parts: 6*sqrt(2) + 10*1 = 18.49

Evaluation of perimeter calculation

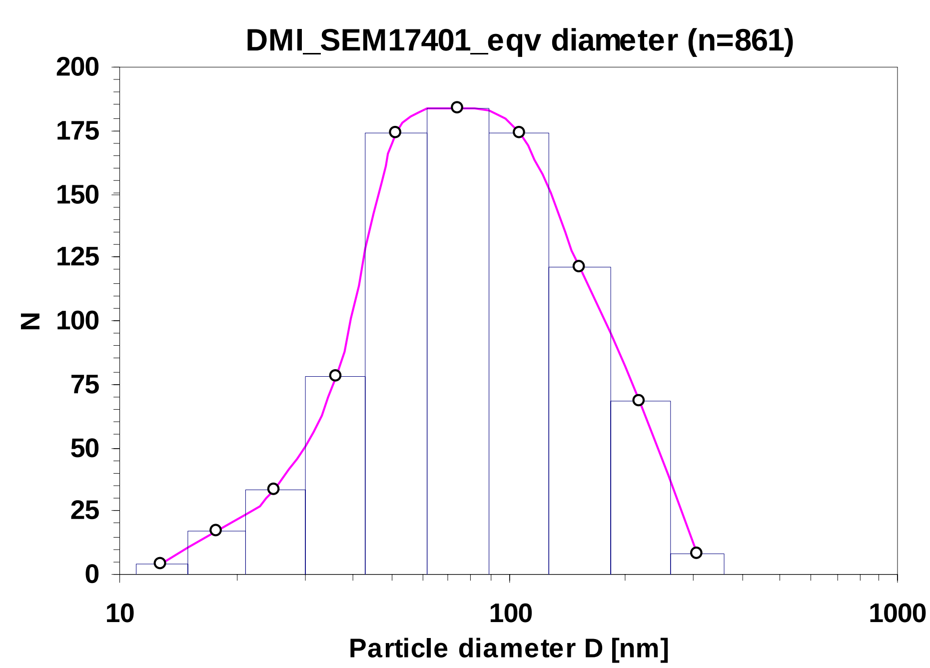


- check for repetitive samples



- minimum p/r should converge to 6.28

Histogram calculation from image analysis of SEM agglomerate populations



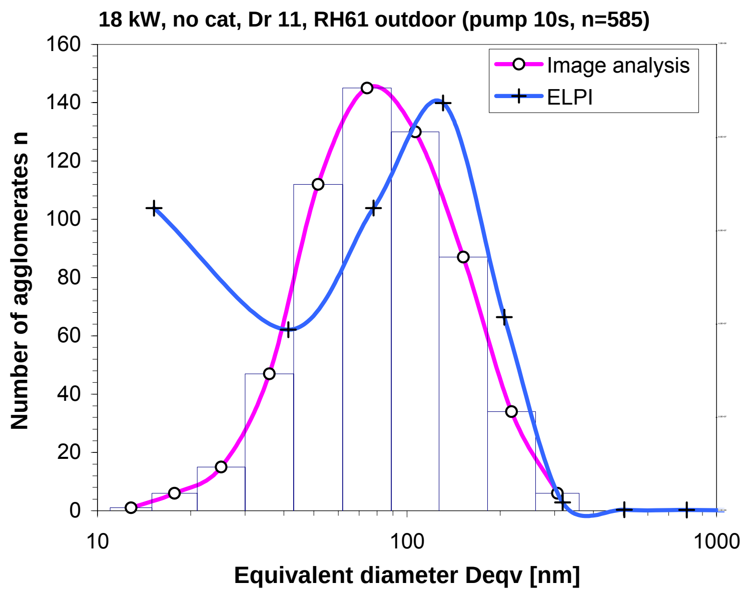
D cut size [nm]	D_g [nm]	dlog D log D(y)/D(x) constant	N number	dN/dlog Dp
11	12.8	0.135	4	29.7
15	17.7	0.146	17	116.3
21	25.1	0.155	33	213.0
30	35.9	0.156	78	498.9
43	51.6	0.159	174	1094.9
62	74.3	0.157	184	1172.0
89	106.3	0.154	174	1126.8
127	152.0	0.156	121	774.3
182	217.5	0.155	68	439.0
260	305.9	0.141	8	56.6
360				
			861	

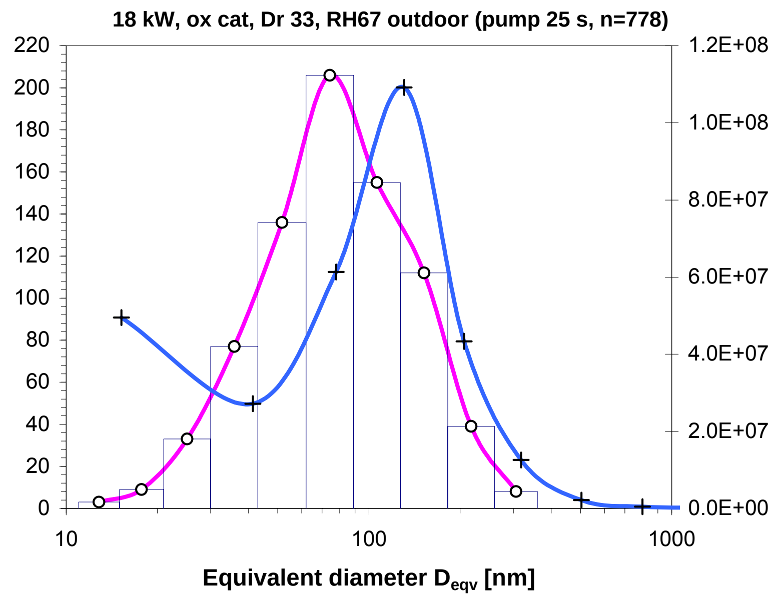
dlog D_p set constant => real N shown in y –axis

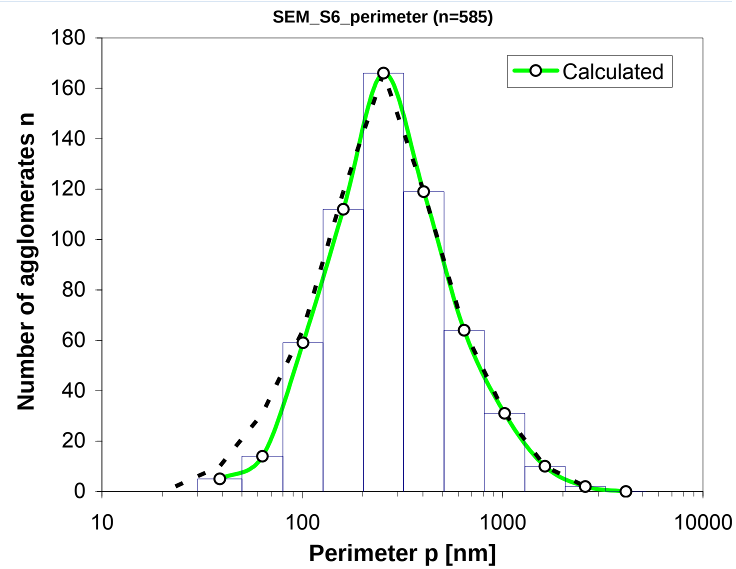
Histograms for N > 400 are calculated for

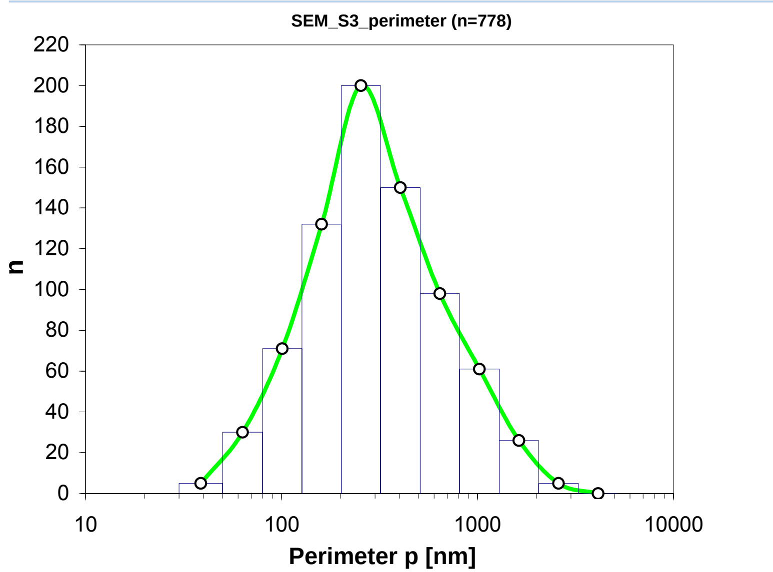
- Equivalent diameter D_{eqv}
- Perimeter *p*
- Area *A*
- Maximum length *L*
- Maximum orthogonal width *W*

Shapes of D_{eqv} and p

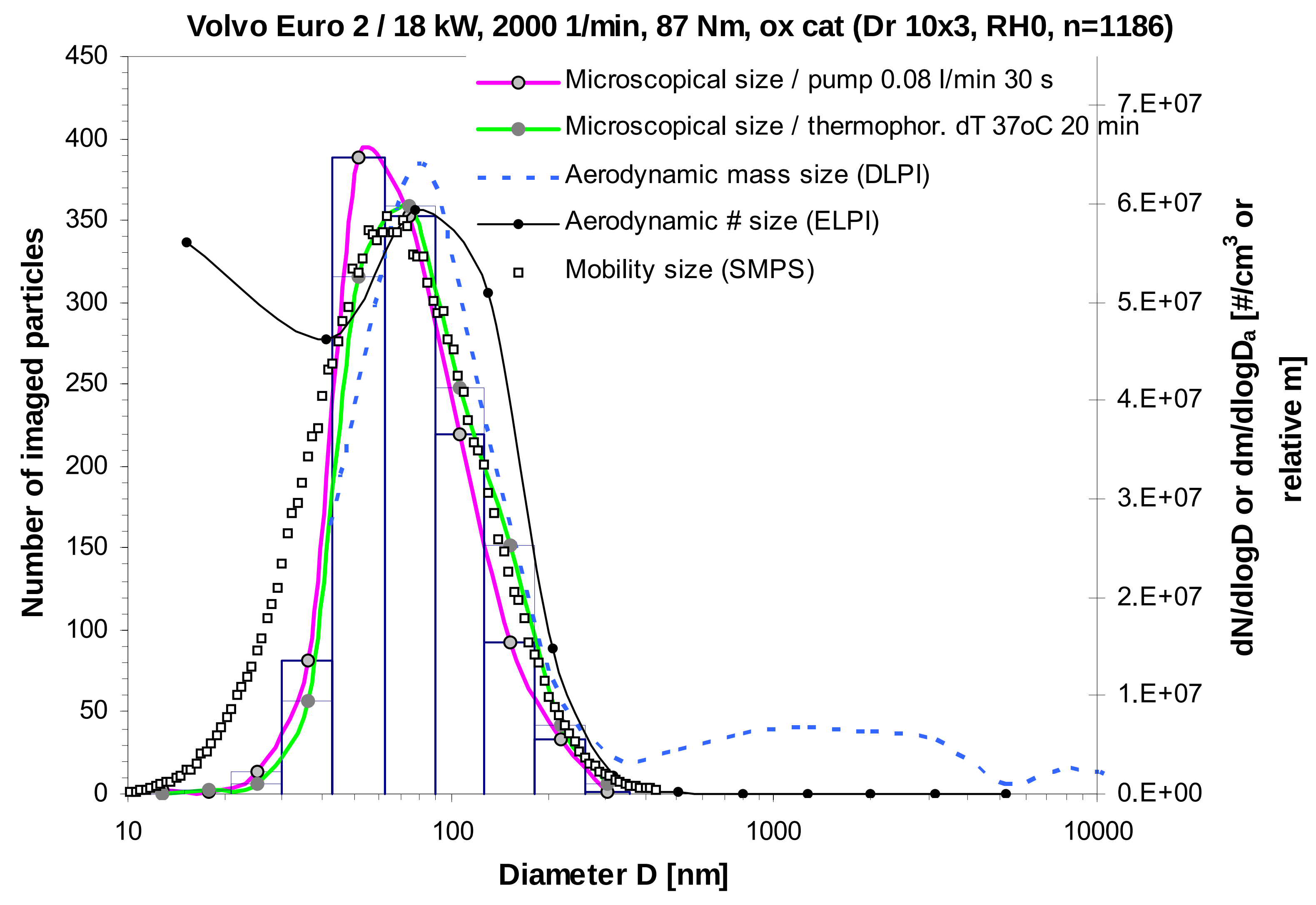








D_{eqv} distributions from thermophoretic and pump sampling vs. aerodynamic and mobility sizes



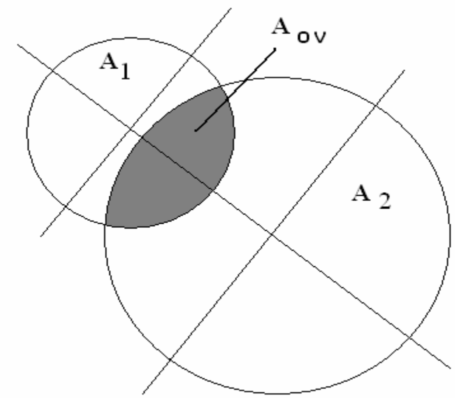
Fractal properties from TEM parameters

$$N = k_g \left(\frac{R_g}{a} \right)^{D_f}$$

$$R_g = \left(\frac{2}{L_a} \sqrt{\frac{D_f + 2}{D_f}} \right)^{-1}$$

$$C_{ov} = \frac{A_{ov}}{\min(A_1, A_2)}$$

- Fractal dimension D_f
- Radius of gyration R_g
- Primary particle radius a
- Fractal pre-factor k_g
- Number of primary particles N
- Overlapping coefficient C_{ov}



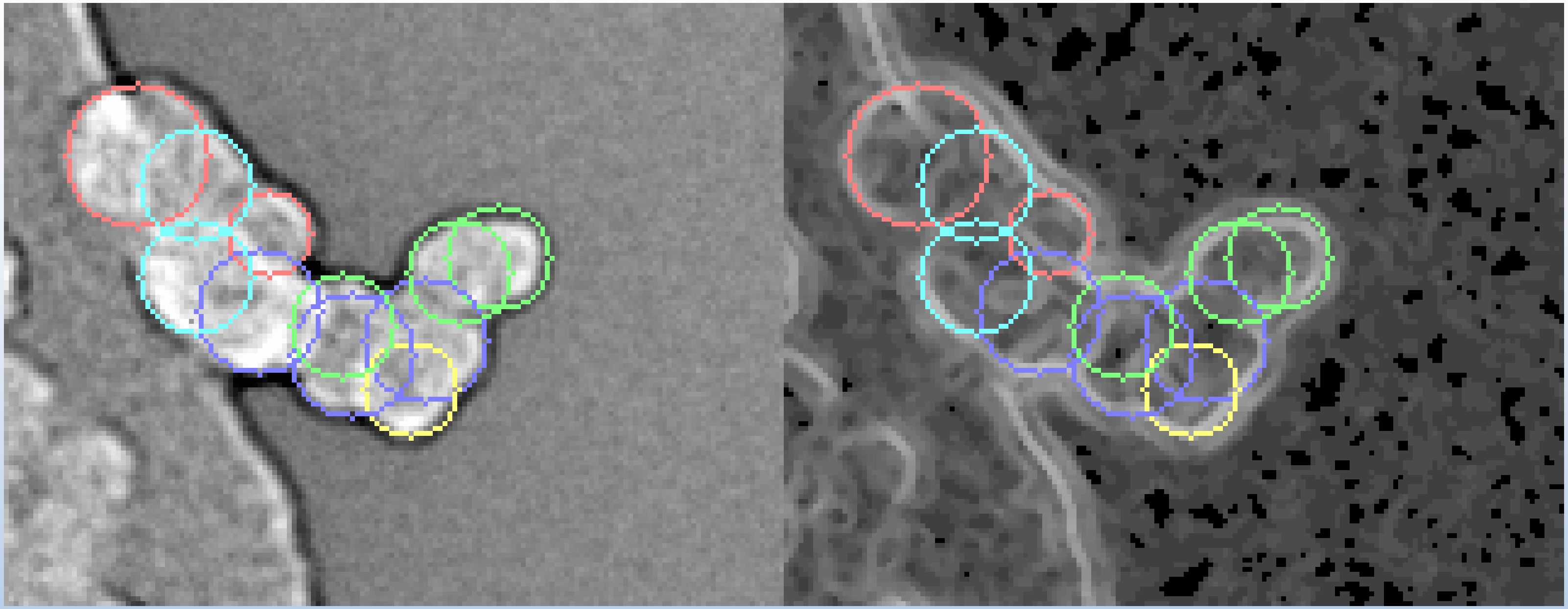
Wentzel, M. et al. , Transmission electron microscopical and aerosol dynamical characterization of soot aerosols *Aerosol Science 34(2003)1347-1370.*

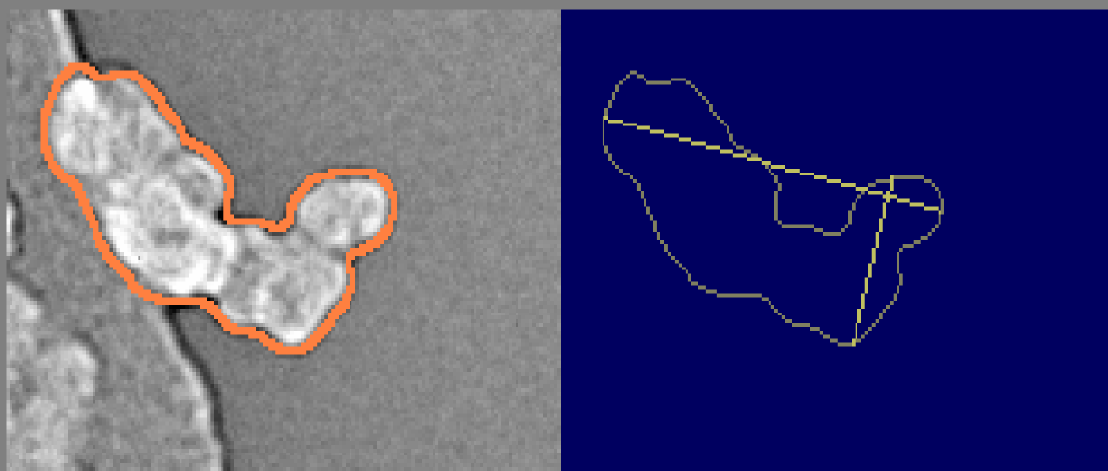
Principles of calculation fractal properties of an agglomerate

- Size and fractal properties are calculated in order: area *A*, max length L_{max}, max orthogonal width W_{max}, perimeter *p*, fractal dimension D_f, radius of gyration R_g, average radius of primary particles *a*, overlapping coefficient C_{ov}, and fractal prefactor k_g.
- Pixels are calibrated to nanometers
- Min and max particle sizes are defined by the operator
- Particle number N calculation is based on *A, a* and C_{ov}
- N calculation is hence sensitive to choice of average particle radius *a*
- C_{ov} calculation takes into account the calculated particle size distribution in an agglomerate
- D_f calculation is based on contour and made by box counting method
- Calculation of R_g, C_{ov} and k_g are made using formulas of /*Mandelbrot 1982, Wentzel et al. 2003/.*

$$N = k_g \left(\frac{R_g}{a} \right)^{D_f} \qquad R_g = \left(\frac{2}{L_a} \sqrt{\frac{D_f + 2}{D_f}} \right)^{-1} \qquad C_{ov} = \frac{A_{ov}}{\min(A_1, A_2)}$$

Calculation of fractal properties from TEM image - 1





$C_{ov} = 0.226$

$D_f = 1.69$

$R_g = 36$ (nm)

$a = 11.5$ (nm)

$N = 11$

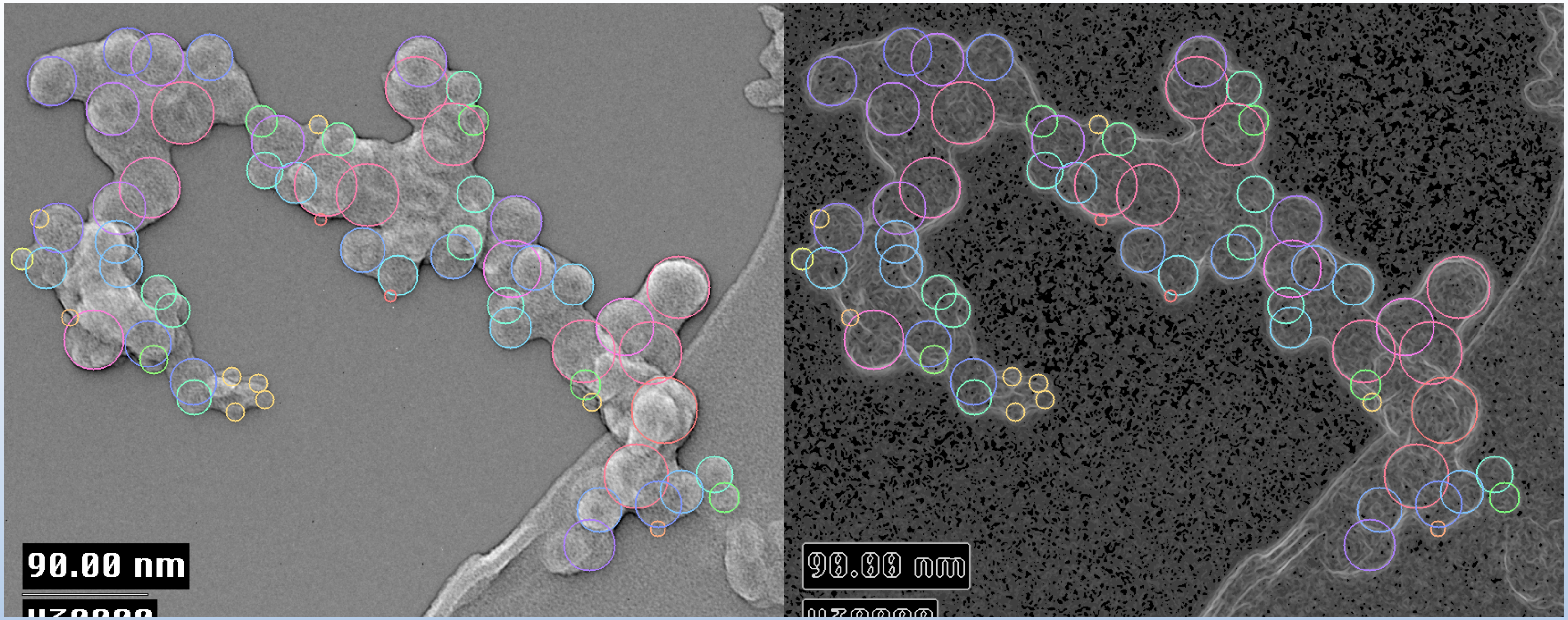
$k_g = 1.6078$

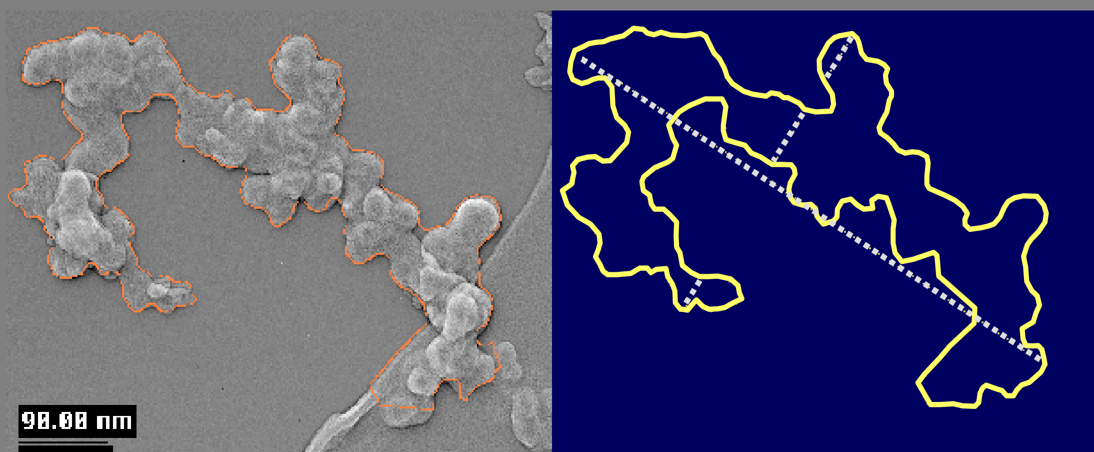
$L_a = 105.9$ (nm)

$p = 325.4$ (nm)

$W = 47.49$ (nm)

Calculation of fractal properties from TEM images - 2



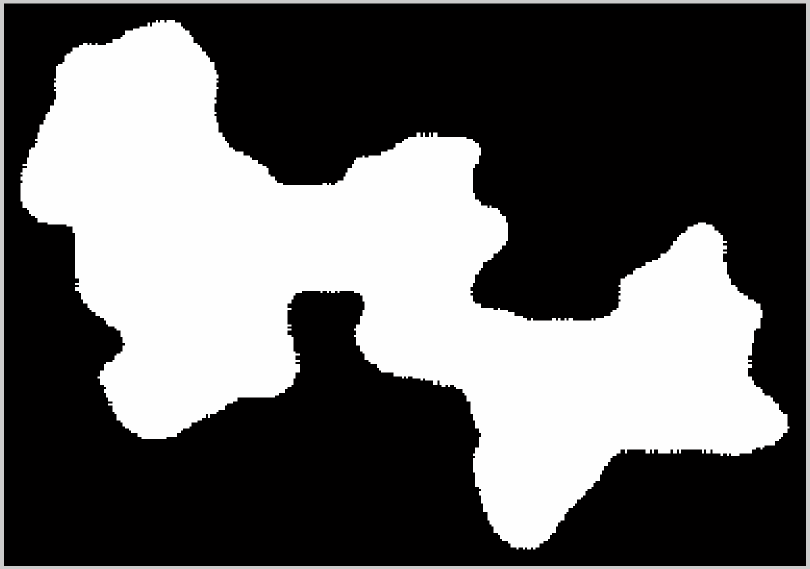


C_{ov} = 0.1848
D_f = 1.6089
R_g = 192 (nm)
a = 13.0263 (nm)
N = 140 (kpl)
K_g = 1.8407
L_a = 576.0877 (nm)
p = 2752.836 (nm)
W = 321.6107 (nm)

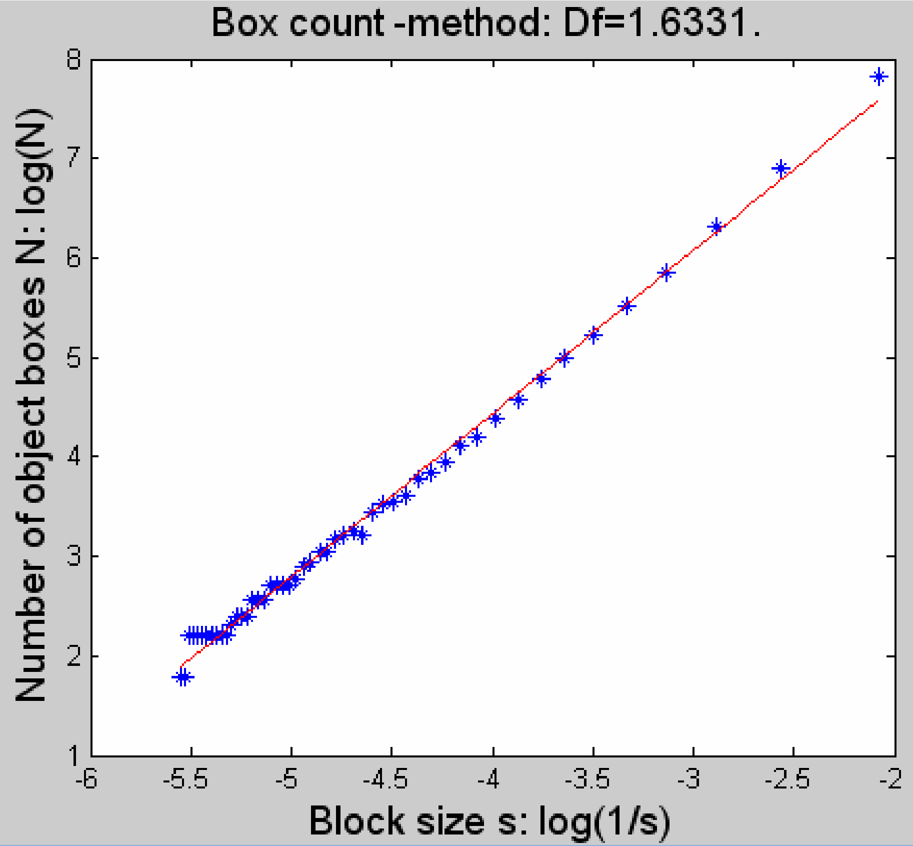
Calculation of fractal dimension D_f

Result is sensitive to the choice of ”average” primary particle diameter a.

TEM-agglomerate
tulos27parametrit.bmp



1.6287	1.6322	1.6316	1.6388	1.6402
1.6287	1.6294	1.632	1.6346	1.6344



Box-counting algorithm y = kx + C

Morphological parameters calculated for two sets of diesel agglomerates from low load point

min	max	Sample: thermophoresis 21 agglomerates
0.153	0.305	C_{ov}
1.547	1.773	D_f (box counting)
26.7	115.4	R_g (nm)
8.1	17.4	a (nm)
8	61	N (#)
1.189	2.208	k_g
78	345	L_{max} (nm)
46	194	W_{max} (nm)
284	1503	p (nm)

min	max	Sample: pump 11 agglomerates
0.128	0.275	C_{ov}
1.527	1.715	D_f (box counting)
56.2	192.3	R_g (nm)
10.1	19.5	a (nm)
12	140	N (#)
1.134	2.148	k_g
168	576	L_{max} (nm)
71	322	W_{max} (nm)
517	2753	p (nm)

18 kW (10 % load,), 2000 1/min, 87 Nm, ox cat (thermodenuder, RH0, Dr 30, raised T for th /ambient T for pump)

Principles of defining primary particle size and calculation of radius *a* size distribution

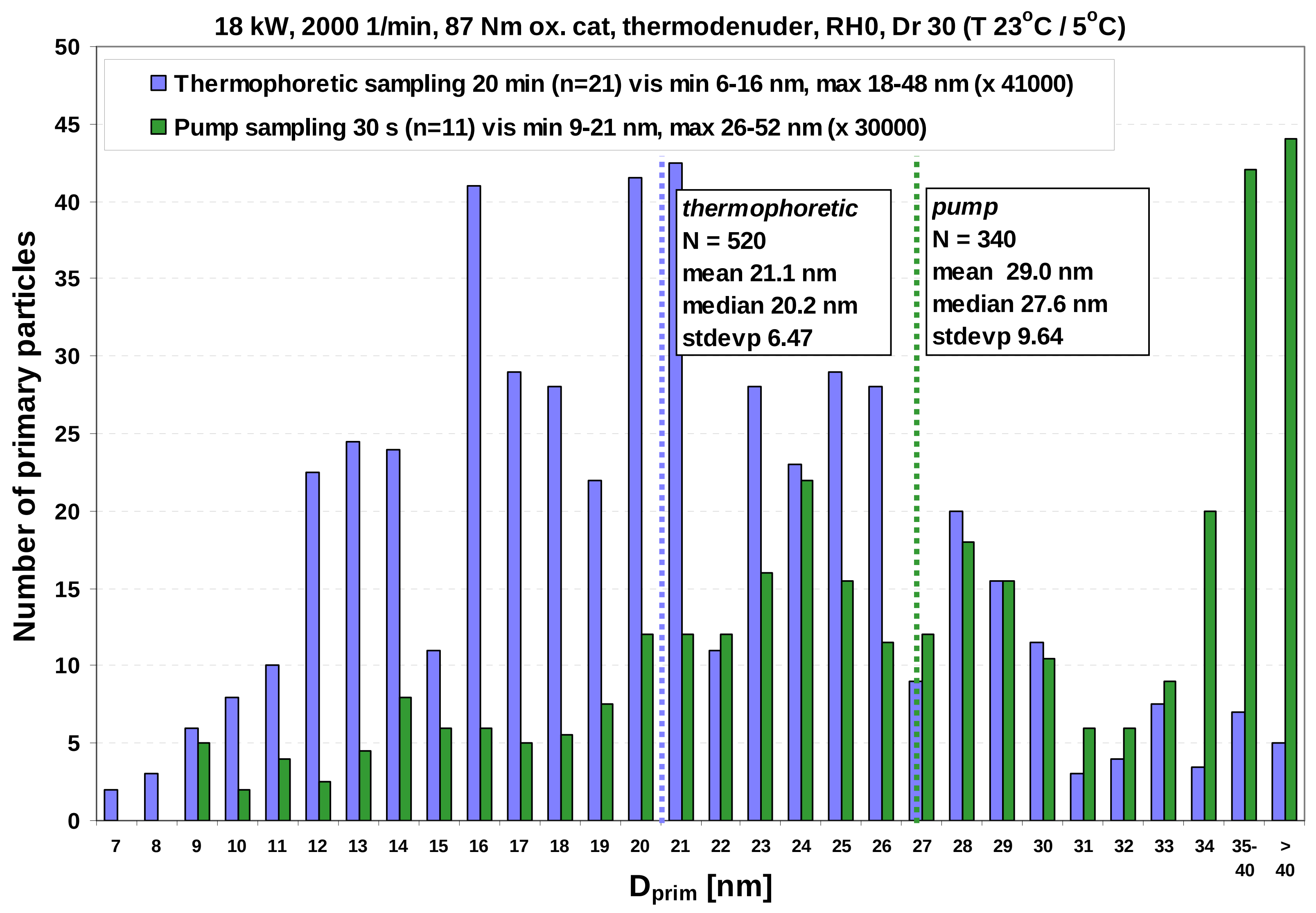
- Contour is determined by thresholding the image; based on operator judgement of the agglomerate edge position
- Primary particle definition is based on a) contour correlation only, or

  Primary particle definition is based on b) correlation between gradient image and fitted primary spheres within operator predefined min – max size range, or
- Primary particles may be defined 100 % manually from the TEM image, using either intensity or gradient image

Primary particle size distributions from two sets of diesel agglomerates by automatic primary particle sizing of the program

Result is sensitive to:

- **image quality** (should be ‘standardized’) or treated manually
- **experience of the analyst** (setting contour & min-max sizes)
- **number of agglomerates** analysed



What is attained, what is not

- **Both sampling principles, thermophoresis and suction seem satisfactory in the sense of representativeness of diesel particle emission.**
- **Matlab 7 + IMP R14 based semi-automatic image analysis method for distributions of diesel agglomerate dimensions A, D_{eqv}, p, L and W from 2D projected images was generated.**
- **Matlab 7 + IMP R14 based semi-automatic image analysis method for fractal properties of diesel agglomerates from 2D projected images was generated.**
- **Method for determination of primary particle size distribution in diesel agglomerates was developed (manual ready, automatic not ready).**
- Trapping mechanisms on carbon coated TEM grids of the sampler are not well analysed.
- Increasing of dT in thermophoretic sampler would be advantageous for sampling times.
- Target for imaging specimens containing volatile matter with environmental electron microscopy ESEM did not work out.
- Optimisation and “standardisation” of EM image quality and its treatment (filtering, thresholding, edge position, grid type, magnification) would be advantageous.
- Calculation of fractal dimension is based on average size of primary particles not size distribution.
- Algorithm for automatically defining primary particle sizes in an agglomerate is not ready; manual definition works.
- Calibration of the method with particles of known size should be made.

Program is available for further development (after translation into English...)

Project organisation

The three year project 2003 – 05 was realised by **VTT Processes, Emission Control**:

Lappi, Maija (project management, coordination)

Tapper, Unto (SEM and TEM microscopy)

Jokiniemi, Jorma (SEM and TEM microscopy, project management)

Vesala, Hannu (instrumental setups)

Tampere University of Technology TUT, Institute of Signal Processing:

Hirvonen, Petri (image analysis program)

TUT

VTT Products and production:

Ehrnsten, Ulla (ESEM microscopy)

Tampere University of Technology, Institute of Physics:

Keskinen, Jorma (project management)

TUT

Project was funded by **TEKES** (**FINE** Program of Finnish Funding Agency for Technology and Innovation), **VTT**, **Dekati Ltd**, **Finnkatalyt Ltd**.

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