High Temperature Condensation Particle Counter (HT-CPC)

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Condensation Particle Counters (CPCs) are commonly used to measure the number concentration of airborne nanoparticles in various applications. A typical CPC consists of three major stages. They are: a saturator where an aerosol sample is saturated with vapour of a fluid e.g. butanol; a condenser where the temperature is reduced, and the vapour becomes supersaturated and the particles grow to optically detectable sizes by condensation of the vapour on particle surfaces; and an optical particle counter (OPC). The working temperature of the saturator and the condenser of a typical CPC are not very far from ambient (e.g. for a Butanol-based CPC, about 35 C and 10 C respectively).

This work is connected with the development of a CPC that is insensitive to volatile particles. The concept is to operate the prospective CPC using an appropriate condensing fluid at such a high temperature that volatile material is evaporated or prevented from condensing. The obvious application is measurement from internal combustion engines, where the European legislated particle number method (PMP) requires a complex system for the removal of volatile material and cooling of the sample to ambient temperature, prior to measurement by a conventional low temperature CPC. If the high temperature CPC is successful, it could replace the PMP system with a single device.

The study involves design, selection of a working fluid, theoretical modelling, construction and testing of a high temperature CPC.

Design and selection of a working fluid

Supersaturation in the condenser of a CPC can be achieved by two different ways: first cooling of a heated saturated flow as exemplified by slowly-diffusing butanol vapour and second, wet-heating of a cool saturated flow as achieved by fast-diffusing water vapour. For a high temperature CPC, the former has been chosen because a high temperature vapour is likely to diffuse slowly. Moreover, since the OPC is attached directly to the heated condenser, it will be easier to thermally isolate it from the condenser.

A fluid for the high temperature CPC should have the operating temperature sufficiently high to avoid homogeneous nucleation of volatile material. Secondly, the mass diffusivity of the fluid must be lower than the thermal diffusivity of the carrier gas. Thirdly, it must be thermally and chemically stable at high temperatures. Fourthly, its vapour pressure at the working temperature must be appropriate, i.e. not too low to grow particles but not too high, in order to minimise fluid waste. Lastly, the fluid ideally must be non-toxic. Furthermore, it would be convenient for instrument transport if the fluid is solid at room temperature.

The question of how hot should a high temperature CPC be is not easy to answer – one approach would be to consider the PMP requirement for removing volatile particles. This states that less than 1% of 30 nm tetracontane ($C_{40}H_{82}$) particles with an inlet concentration of at least 10^4 cm^{-3} should be detected. This concentration of particles, when fully evaporated, would give a vapour pressure equivalent to that of saturated tetracontane at about 90 ℃. Though of course it depends on the actual sample composition, it seems plausible that a CPC condenser temperature of 150 C or more would be satisfactory, especially as in most situations hot dilution will be required to ensure single particle count mode from the OPC.

Di-Ethyl-Hexyl-Sebacate (DEHS) has been selected as a fluid candidate for a high temperature CPC because its boiling point is sufficiently high. Although DEHS was found to react appreciably with oxygen at elevated temperatures, using nitrogen as the carrier gas allows a significant test duration, but not sufficient for a practical instrument. The mass diffusivity of DEHS in nitrogen is significantly smaller than thermal diffusivity of nitrogen, making it suitable for a cooling type condenser. DEHS vapour pressure is low at high temperatures, i.e. ~0.3% of ambient at 230 ℃. Moreover, it is non-toxic and commonly available.

Typical operating conditions for the HT-CPC are shown in figure 1. The saturator and condenser temperatures are at 230℃ and 180℃ respectively, the total flowrate is 0.366 l/min with an aerosol sample of 6% of the total flowrate introduced at the bottom of the condenser centre. Particle-free nitrogen gas is used as the carrier gas.

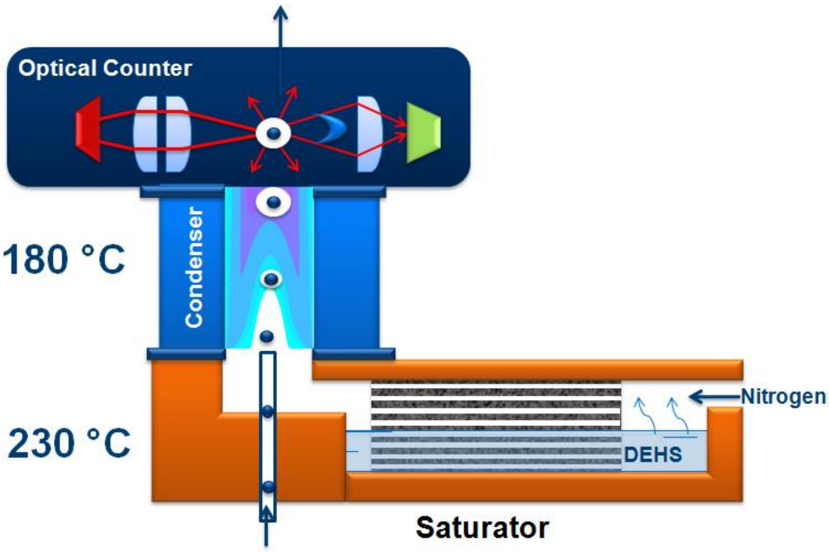

Figure 1. Typical operating conditions for the HT-CPC

The supersaturated region in the condenser where particles are grown, is modelled by numerically solving the heat and mass transfer equations based on the finite difference method. The model was found to be in good agreement with an alternative model due to Stolzenburg and McMurry (1991).

Assuming that all activated particles grow to detectable sizes, the counting efficiency is equal to the activation efficiency. Using the contour of Kelvin-equivalent activation diameter and particle concentration profile due to diffusion, the activation efficiency is the number of activated particles divided by the total inlet particles.

The simulations suggest that the HT-CPC will be able to grow and detect fine solid particles. For the typical embodiment, the saturation ratio along the condenser's centreline is shown in Figure 2. Particle growth was modelled by the mass and heat balance at the droplet surface, following the approach of Ahn and Liu (1990). The growth profile of a 23 nm solid particle is shown in Figure 3.

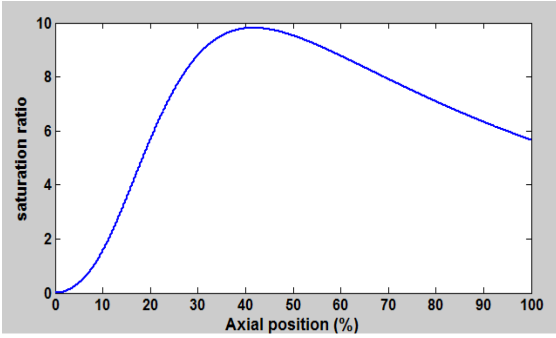

Figure 2. Saturation ratio along the centreline of the condenser.

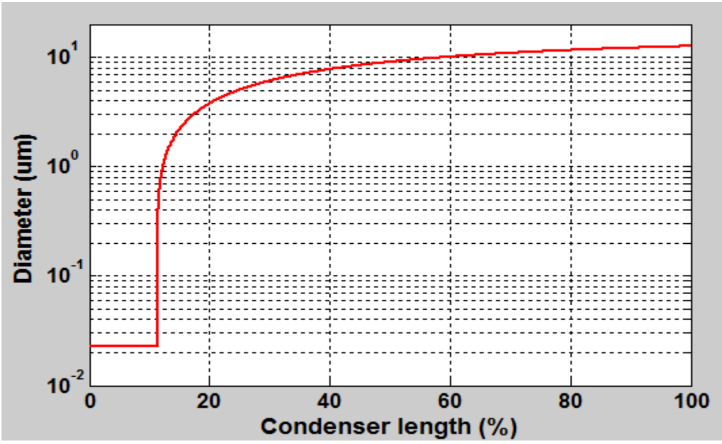

Figure 3. Particle growth along the condenser.

Experimental Study

NaCl particles classified by a Differential Mobility Analyzer (DMA) were introduced to the HT-CPC when the saturator and condenser were kept at 215℃ and 160℃ respectively. Using a TSI 3775 butanol CPC as a reference, the measured and theoretical counting efficiency of the high temperature CPC as a function of particle electrical mobility diameter is shown in figure 4.

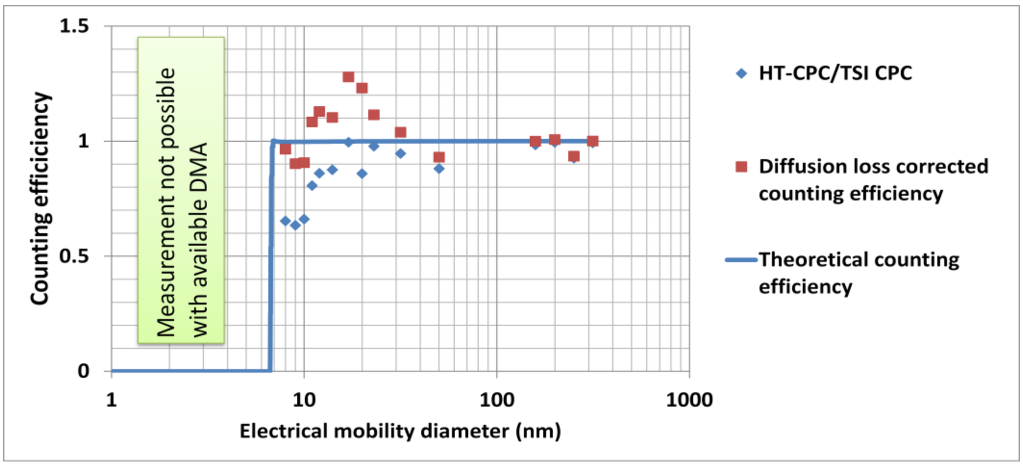

Figure 4. Counting efficiency of the HT-CPC

When the saturator and condenser were kept at 230 ℃ and 180 ℃ respectively, tetracontane particles were introduced to the HT-CPC without sample pre-heating. It was found that about 99% of tetracontane particles of electrical mobility diameter 7 – 310 nm at concentration higher than 10^4 #/cc were not counted while nearly all NaCl particles were counted. Particle concentration measured by the HT-CPC corrected for diffusion loss in the sampling line and by the reference butanol CPC is shown in figure 5 and the counting efficiency of tetracontane particles is shown in figure 6.

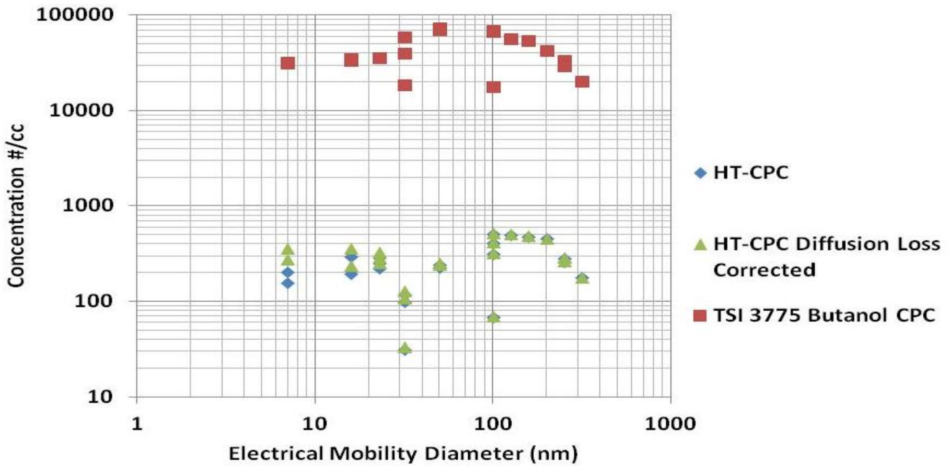

Figure 5. Tetracontane particle concentration as measured by the HT-CPC and the reference butanol CPC

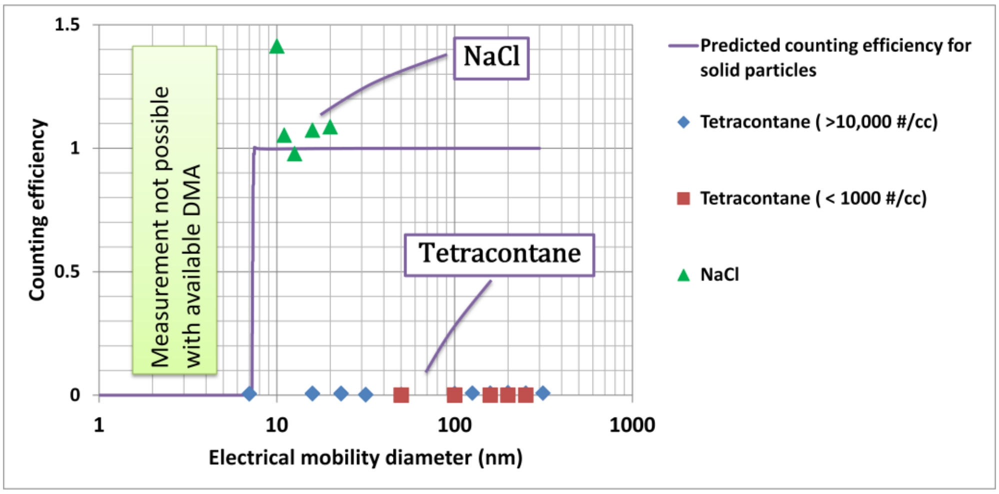

Figure 6. Counting efficiency of tetracontane particles at high concentration (> 10^4 #/cc) and low concentration (< 10^3 #/cc)

Conclusions

A HT-CPC using Di-Ethylhexyl-Sebacate (DEHS) as the working fluid running at 230/180 ^{0}C has been built and tested. The measured counting efficiency for NaCl particles (solid particles) agrees well with model predictions. Tetracontane particles of electrical mobility diameter range 7nm – 310nm at concentration higher than 10^4 #/cc were removed with about 99% efficiency, even without sample pre-heating or dilution. DEHS is not suitable due to thermal decomposition. However, the DEHS CPC has successfully demonstrated the HT-CPC concept, though not as yet on combustion-generated particles.

References:

Stolzenburg, M. R, and McMurry, P. H. (1991) *An Ultrafine Aerosol Condensation Nucleus Counter,* Aerosol Science and Technology, 14: 1, 48 - 65.

Ahn, K.-H., and Liu, B. Y. H. (1990) *Particle Activation and Droplet Growth Processes in Condensation Nucleus Counter. I. Theoretical Background,* J. Aerosol Sci. 21: 2, 249 - 261.

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ETH Zürich

Outline

- Motivation
- The Condensation Particle Counter (CPC)
  - Principle
- The High Temperature CPC (HT-CPC)
  - Desirable characteristics
  - Working fluid
  - Modelling
- Experiments
- Conclusions

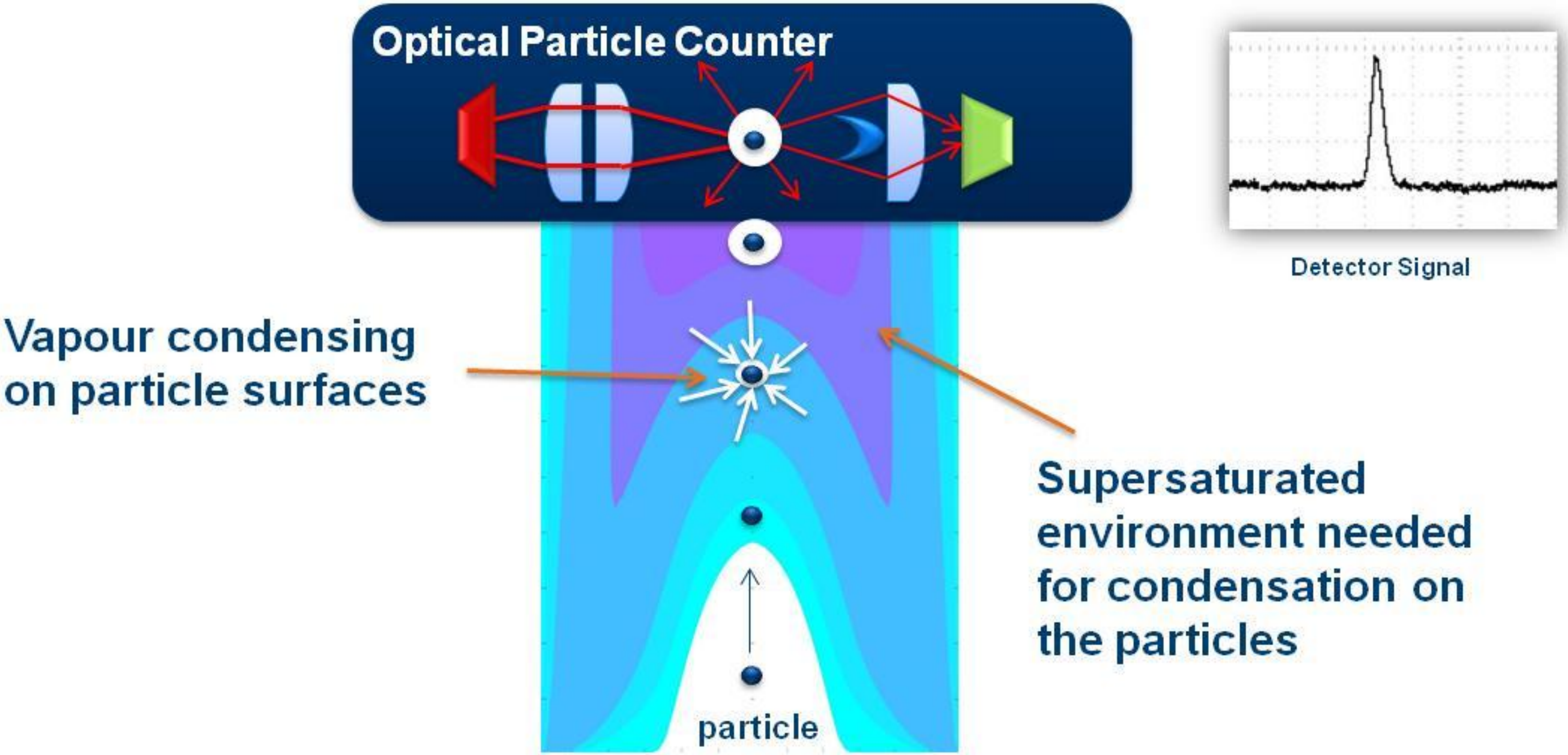
Motivation

- European legislated particle number method ("PMP") requires a complex system for the removal of volatile material, and cooling of the sample to ambient temperature, prior to measurement by a conventional CPC.

- This work is concerned with development of a HT-CPC that is insensitive to volatile particles (even though the PMP legislation would not allow the use of such an instrument as written), and permits "hot" inlet conditions. Whether or not such an instrument has relevance to PMP is not addressed here.

The CPC - Principle

The essence of a CPC is to grow nanoparticles to a size where they can be optically detected.



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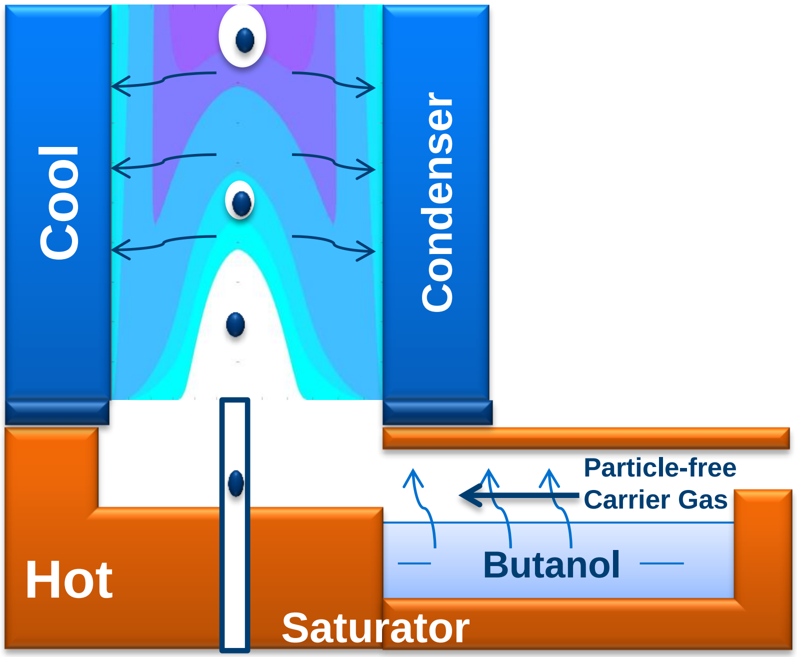
How does a CPC create supersaturation?

Butanol CPC

- Slowly diffusing butanol molecules
- Cooling is faster than Butanol diffusion loss to the wall

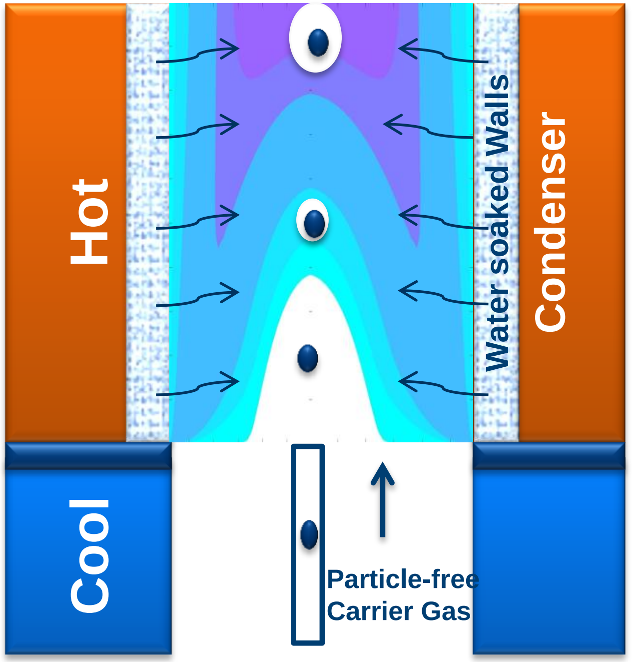
Mass diffusivity$_{\text{butanol-air}}$ < Thermal diffusivity$_{\text{air}}$



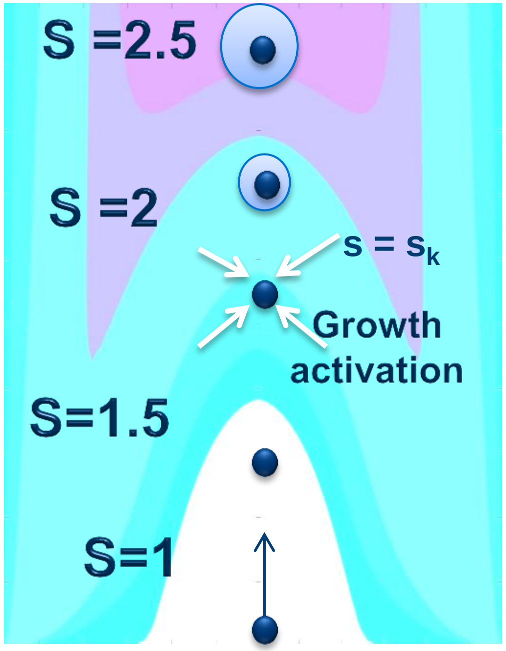
Water CPC

- Fast diffusing water molecules
- Heating is slow than water diffusion to the flow

Mass diffusivity$_{\text{water-air}}$ > Thermal diffusivity$_{\text{air}}$



The CPC – Particle growth activation



Particle diameter d_k

The diameter (d_k) of a droplet of the pure condensing species in equilibrium with its vapour, at saturation ratio S and temperature T, is given by the Kelvin equation:

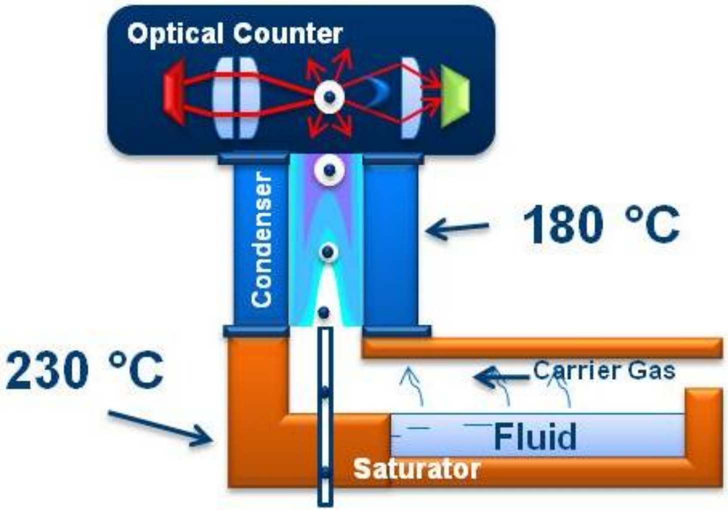
$$d_k = \frac{4\gamma M}{\rho RT \ln S}$$

γ = liquid surface tension
M = molecular mass
ρ = liquid density
R = universal gas constant

This is equivalent to the **Activation Diameter** of a particle readily wetted by the condensing vapour.

Activation diameter will be larger for particles not readily wetted by the vapour.

The HT-CPC – Requirements



Cooling Type Condenser

- High boiling point fluids are likely to have low mass diffusivity

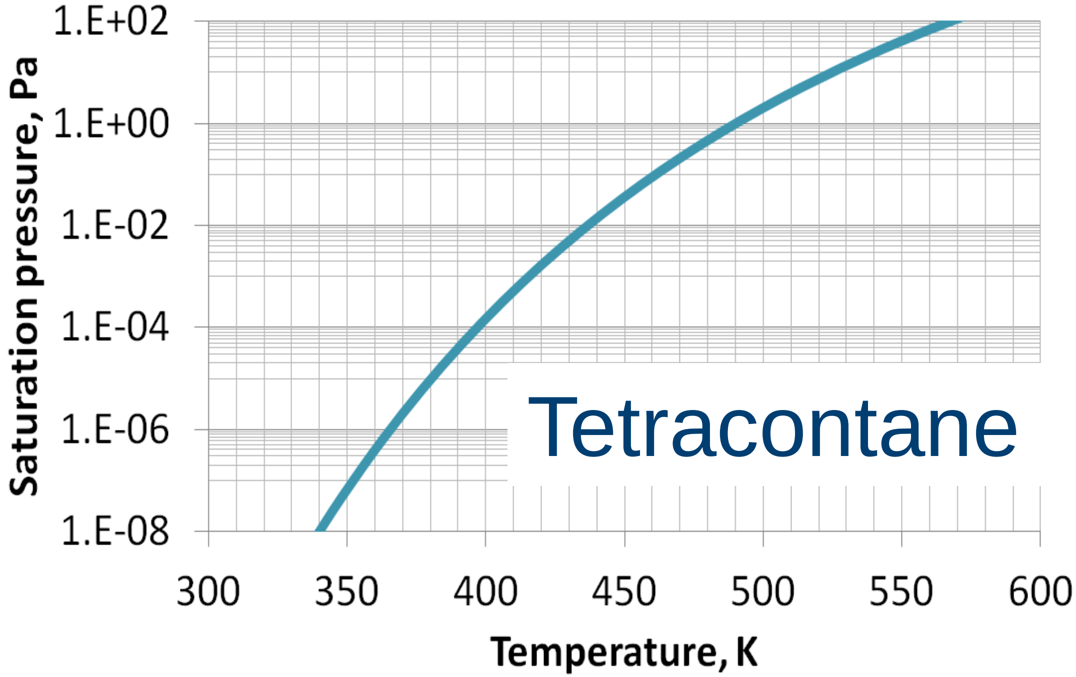
- Optical Counter easier to keep at a safe temperature

Desirable characteristics

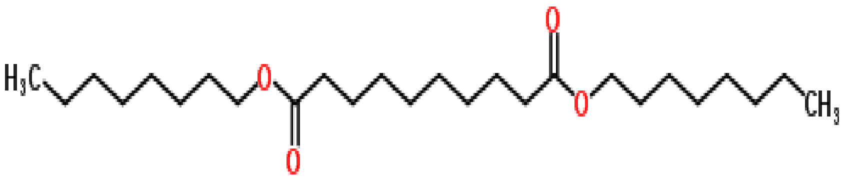
- Operating temperature sufficiently high to avoid nucleation of all volatile material, without the need for upstream removal.
- Mass diffusivity of fluid < thermal diffusivity of carrier gas
- Fluid stable at high temp, and in presence of oxygen etc. Non-toxic.
- Fluid vapour pressure appropriate at working temperature
- (Fluid solid at room temperature – no more CPC transport issues!)

How hot should a HT-CPC be?

- Difficult question! (Even without considering (hot) dilution in order to maintain single particle count mode.)
- Experience suggests that at >= 150 ºC, no nucleation particles from a real-life engine sample will survive.
- For example (borrowing the PMP tetracontane test) if 10^4 #/cc $C_{40}H_{82}$ particles with d_p = 30 nm are fully vapourised, $p_{sat} \approx 4.5\times10^{-7}$ Pa, corresponding to $t_{sat} \approx$ 90 ºC (≈ 360K).
- Perhaps 150 ºC would be "safe" ($p_{sat} \approx 4\times10^{-3}$ Pa)



First test fluid - Di-Ethyl-Hexyl-Sebacate (DEHS)



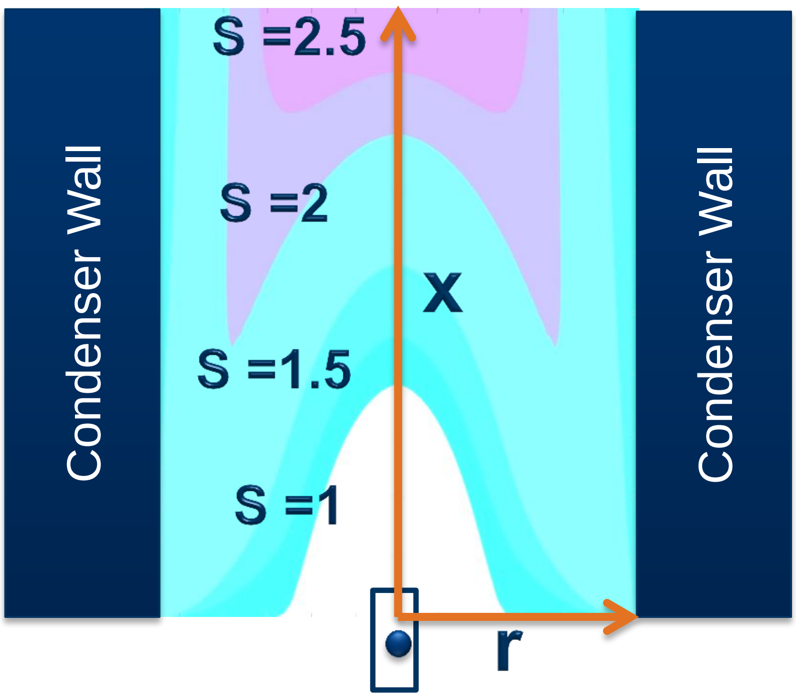
$C_{26}H_{50}O_4$

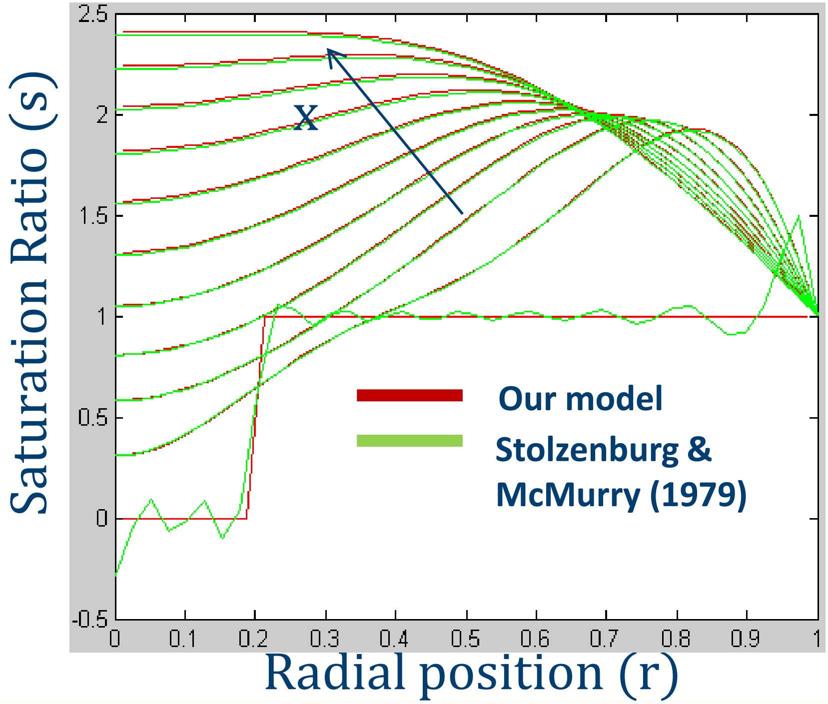
- High boiling point ~ 377°C
- Mass diffusivity ($D_{DEHS\text{-}N2}$) = 0.069 cm²/s (predicted)
- Thermal diffusivity (of N_2) (α) = 0.47 cm²/s .
- Vapour Pressure at 230 °C is ~0.3 kPa (i.e. ~0.3% of ambient)
  (For butanol at 40 °C ~ 1.7%)
- Non-toxic
- Unfortunately, DEHS was found to react appreciably with oxygen at elevated temperatures. Using nitrogen as the carrier gas allows a significant test duration but not sufficient for a practical instrument

Modelling – Saturation ratio

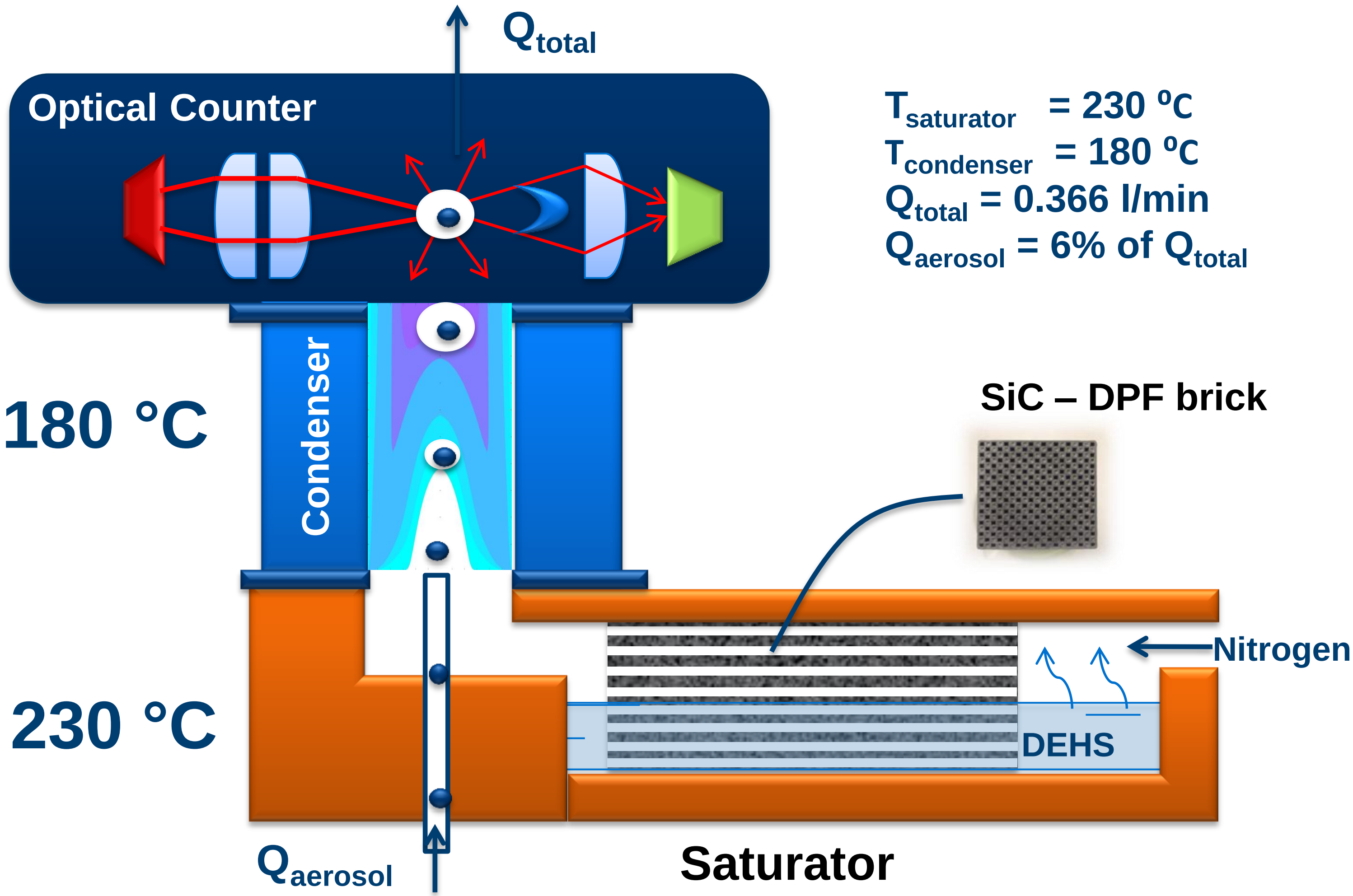
- The model we have developed solves heat and vapour transfer in the condenser for the profiles of temperature, vapour pressure and hence saturation ratio.

(Comparison – using Butanol as the working fluid, $T_{saturator} = 35\ ^oC$, $T_{condenser} = 10\ ^oC$)





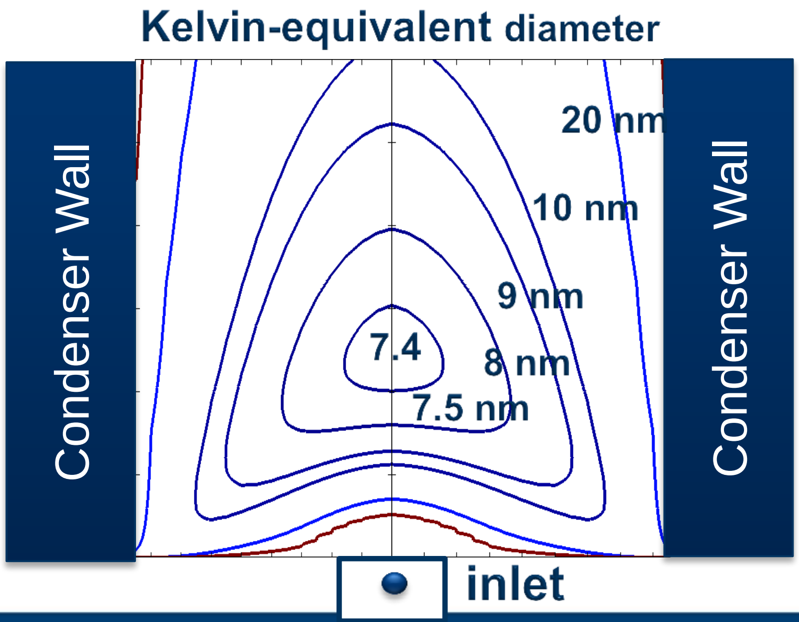
Typical operating conditions

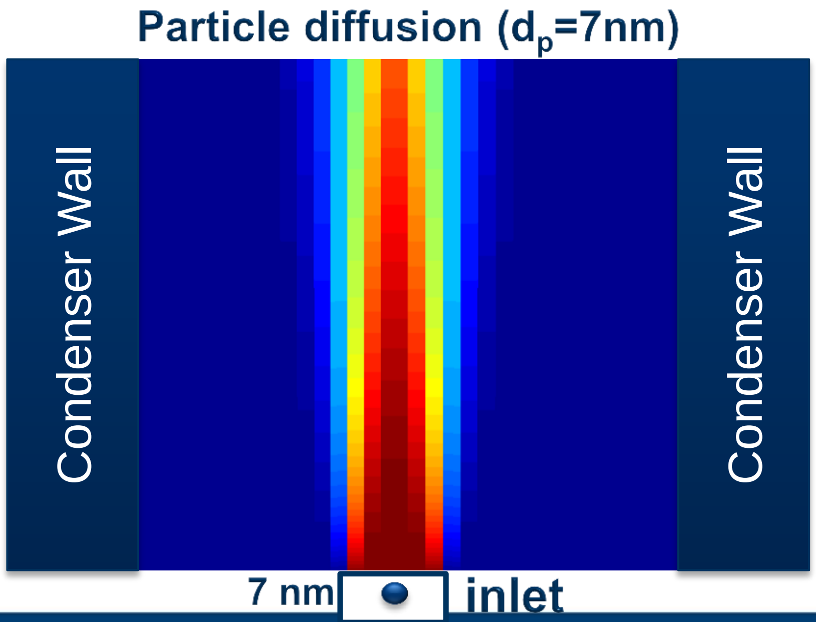


$T_{saturator}$ = 230 °C
$T_{condenser}$ = 180 °C
Q_{total} = 0.366 l/min
$Q_{aerosol}$ = 6% of Q_{total}

Modelling – Counting efficiency

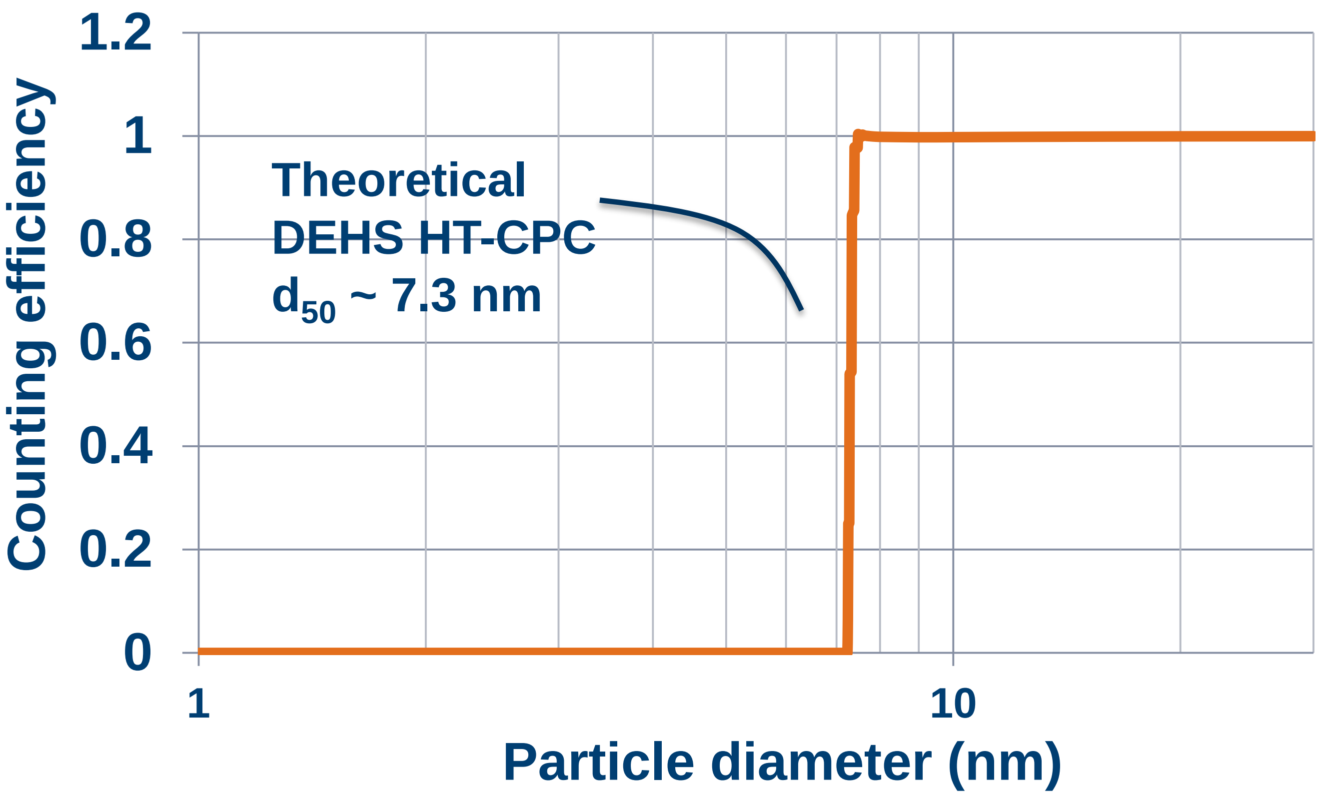
- Assuming that all activated particles grow to detectable sizes, the counting efficiency is equal to the activation efficiency.
- Using the contour of Kelvin-equivalent activation diameter and particle concentration profile due to diffusion, the activation efficiency is #activated particles / #total inlet particles.





Modelling – Counting efficiency

Theoretical counting efficiency for solid particles



$T_{saturator}$ = 230 ^oC
$T_{condenser}$ = 180 ^oC
Q_{total} = 0.366 l/min
$Q_{aerosol}$ = 6% of Q_{total}

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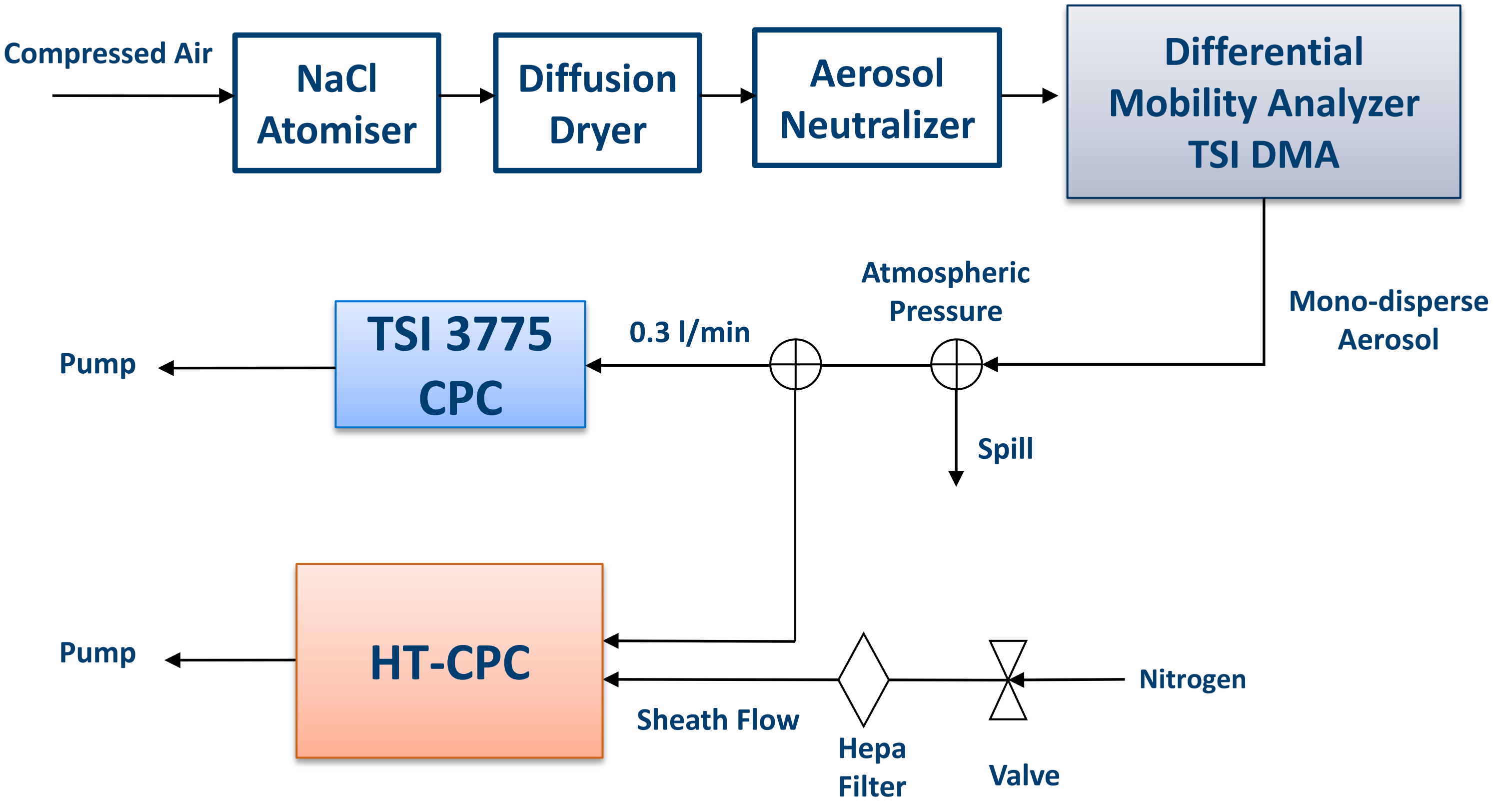
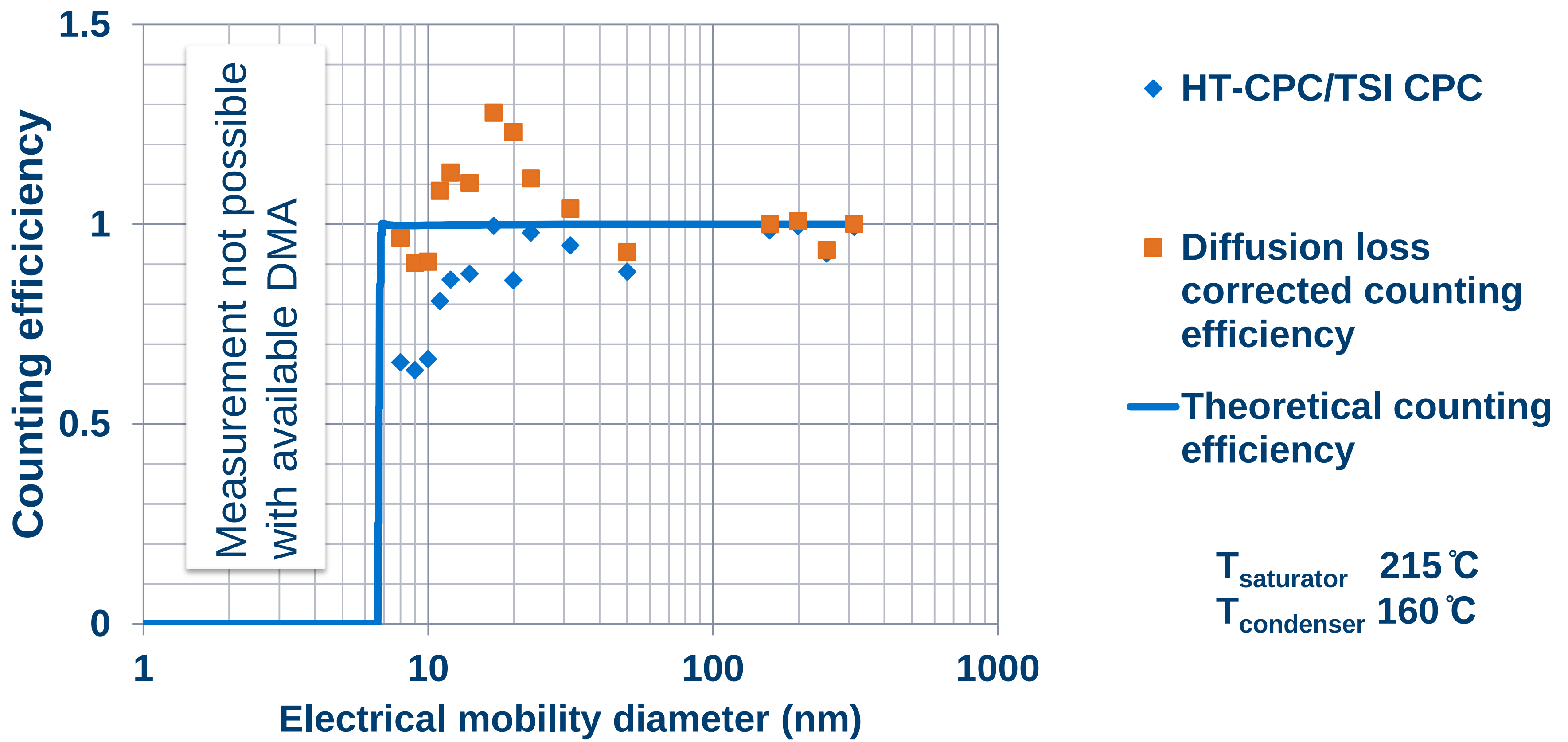
Experiment

Experimental Set-up



Experiment - Counting efficiency of solid particles

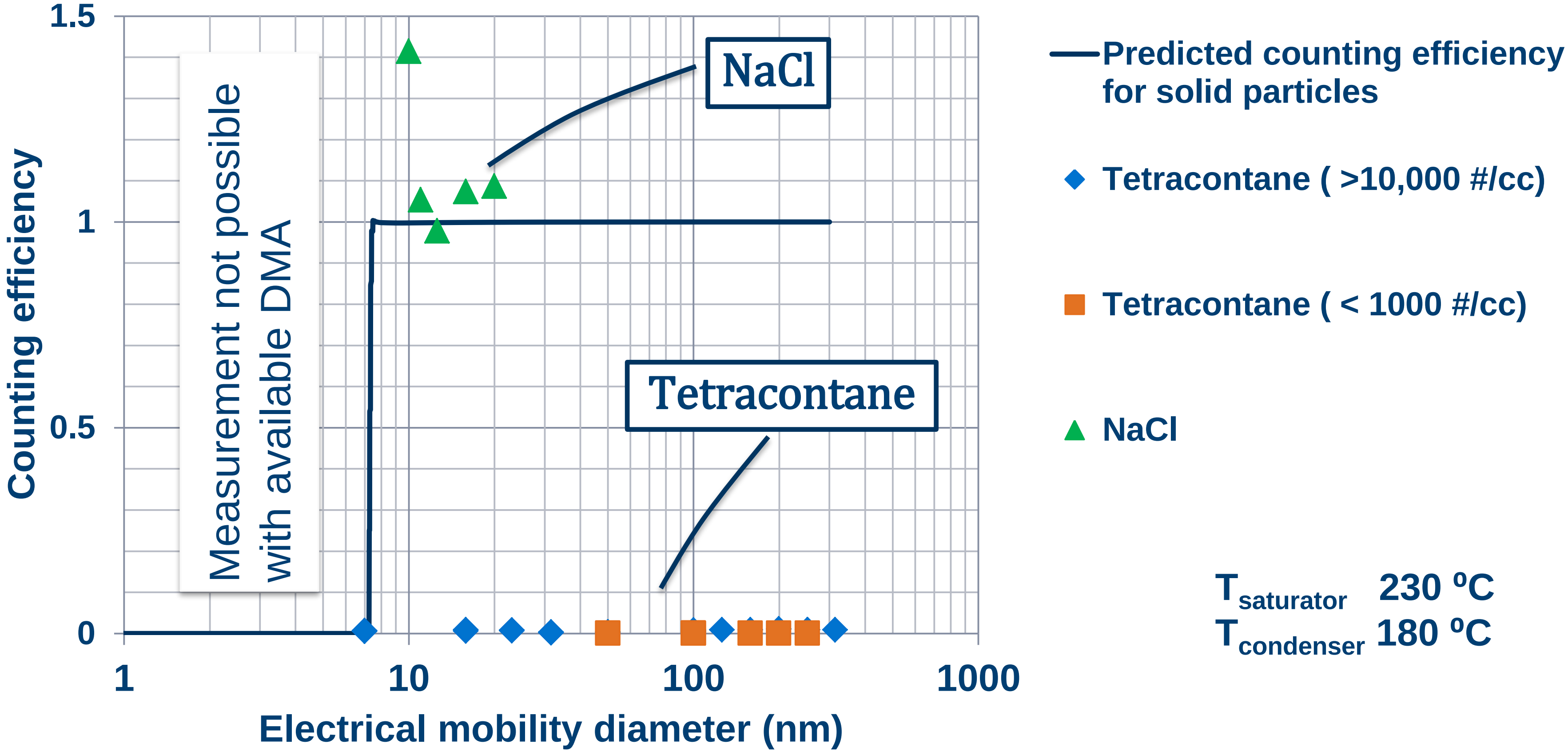
Counting efficiency of solid particles (NaCl)



$T_{saturator}$ 215 ℃
$T_{condenser}$ 160 ℃

Experiments – Tetracontane Particles

Counting Efficiency (data corrected for diffusion losses and counting efficiency)



$T_{saturator}$ 230 ºC
$T_{condenser}$ 180 ºC

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Thoughts on alternative working fluids

- It seems that pure hydrocarbons/alcohols are unlikely to be stable enough at the temperatures required – though as with IC engine lubricating oils, suitable additives might result in an acceptably stable fluid.
- Other possibilities could be:
  - Silicone oils (siloxanes), DC705
  - Perflurocarbons (e.g. perfluorohexadecane, $C_{16}F_{34}$)
  - Perfluorotrihexylamine ($C_{18}F_{39}N$), Fluorinert FC-70 (a 3M “electronic liquid”)
- These are cheap, mass-production compounds.

Conclusions

- A HT-CPC using Di-Ethylhexyl-Sebacate (DEHS) as the working fluid running at 230/180 ^{o}C has been built and tested.
- The measured counting efficiency for NaCl particles (solid particles) agrees well with model predictions.
- Tetracontane particles of electrical mobility diameter range 7nm – 310nm @ concentration higher than 10^4 #/cc were removed with about 99% efficiency, even without sample pre-heating or dilution.
- DEHS is not suitable due to thermal decomposition
- However, the DEHS CPC has successfully demonstrated the HT-CPC concept, though not as yet on combustion-generated particles.

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Thank you

High Temperature Condensation Particle Counter

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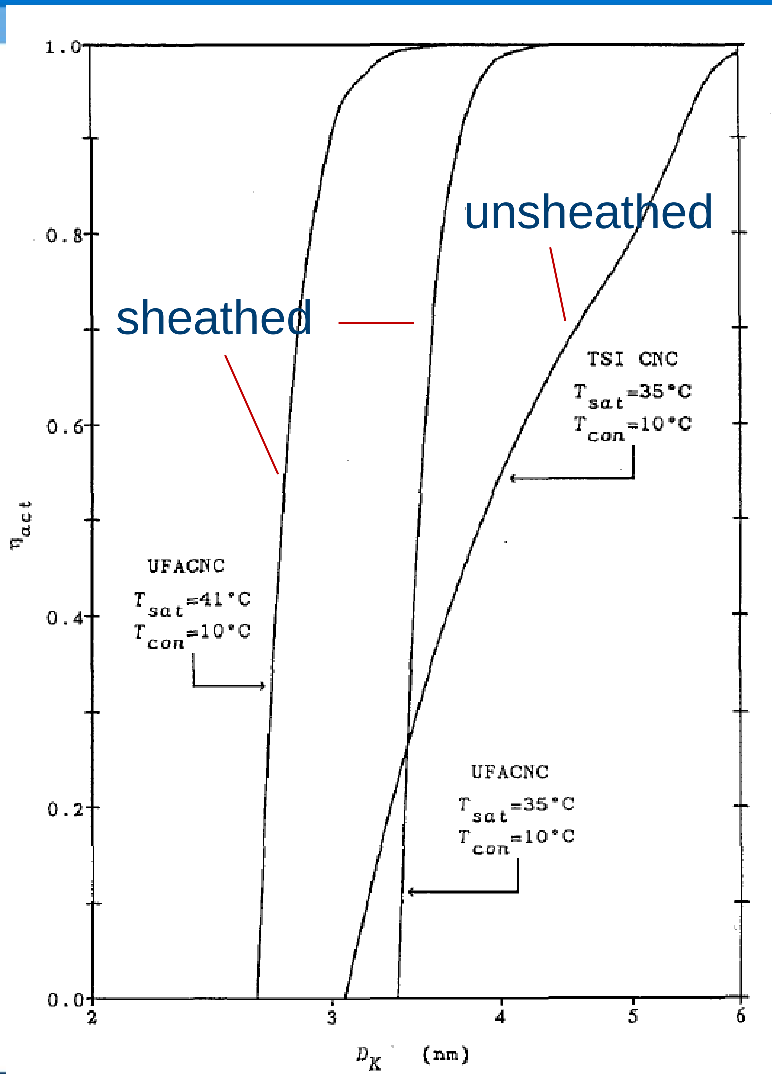
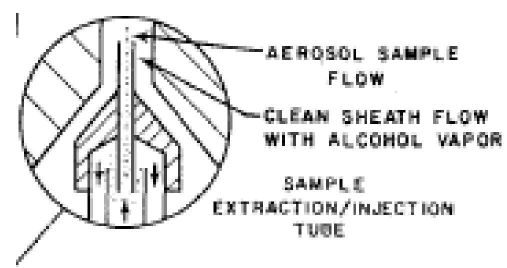
Additional Slides

- Additional slides

Butanol CPC theoretical counting efficiency



Theoretical counting efficiency of the a butanol ultrafine CPC.

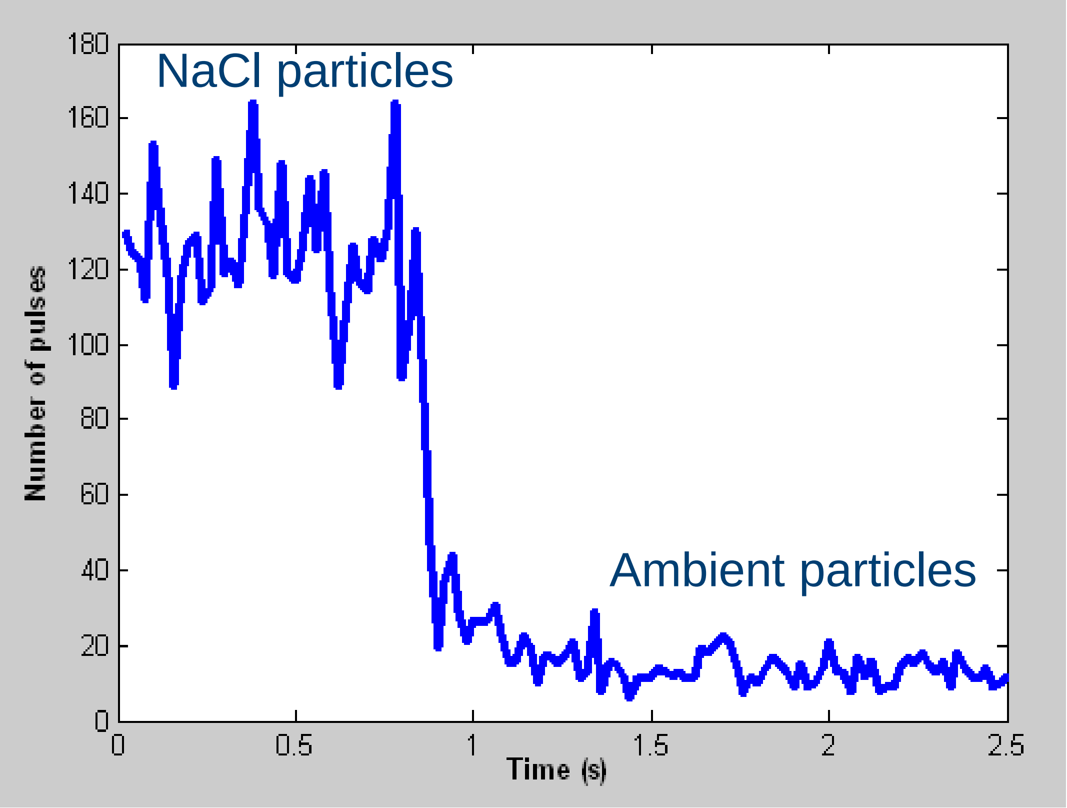


Steep step cut off due to sheath flow

Stolzenburg and McMurry (1991) , An Ultrafine Aeriosol Condensation Nucleus Counter, Aerosol Sci and Technology, 14:1, 48 - 65

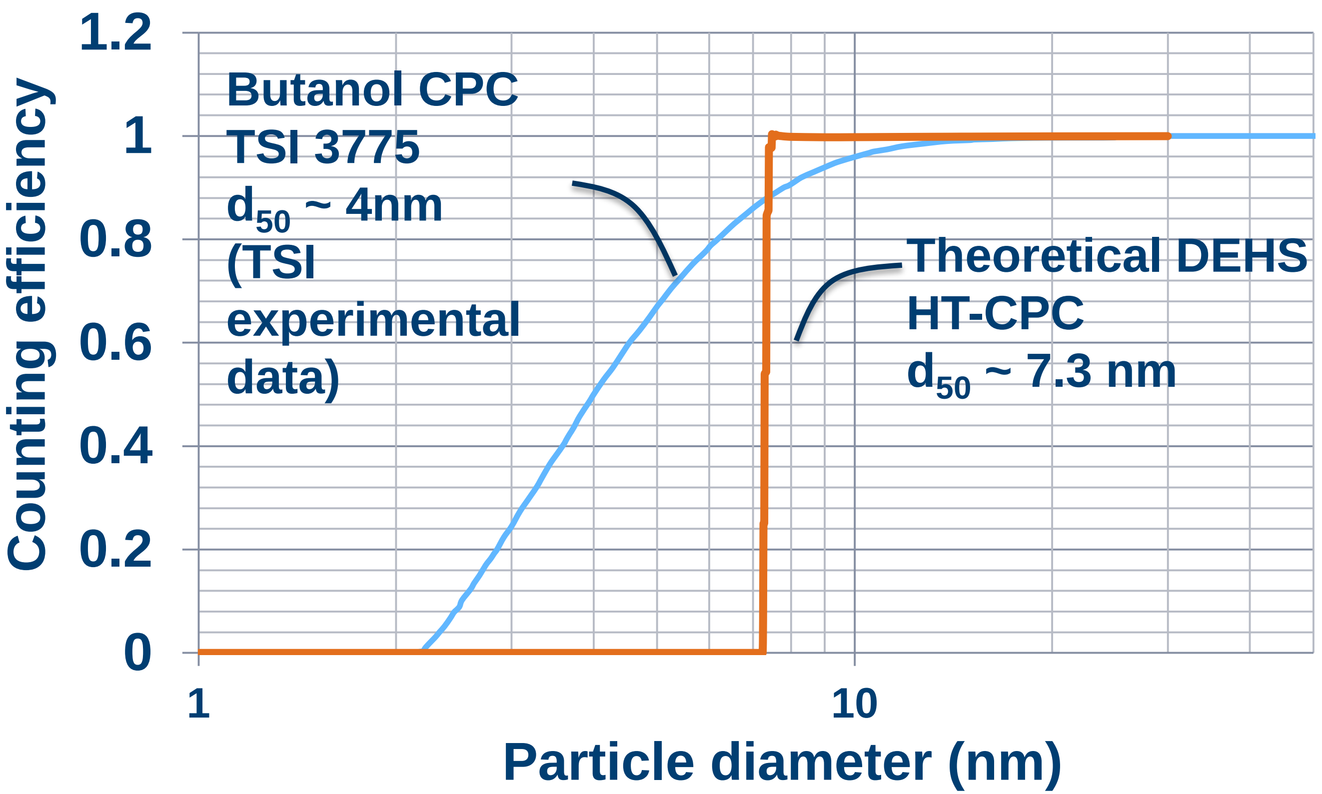
Time response measurement

- Response to a step decrease in particle concentration at sampling period of 50 ms
- Time response of the HT-CPC depends on particle concentration, flowrate and sampling period. The T_{90-10} should be very fast, < 50 ms (for flowrate 1l/min).



Modelling – Counting efficiency

Theoretical counting efficiency for solid particles



$T_{saturator}$ = 230 ºC
$T_{condenser}$ = 180 ºC
Q_{total} = 0.366 l/min
$Q_{aerosol}$ = 6% of Q_{total}

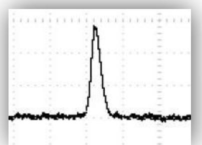
Modelling – Volatile evaporation

- Volatile evaporation in the entire continuum, transition and free molecule regimes is modelled by heat and mass balance on the particle surface.*

- Tetracontane ($C_{40}H_{82}$) as the challenging particle

* Fuchs and Sutugin (1970)

the High Temp-CPC System



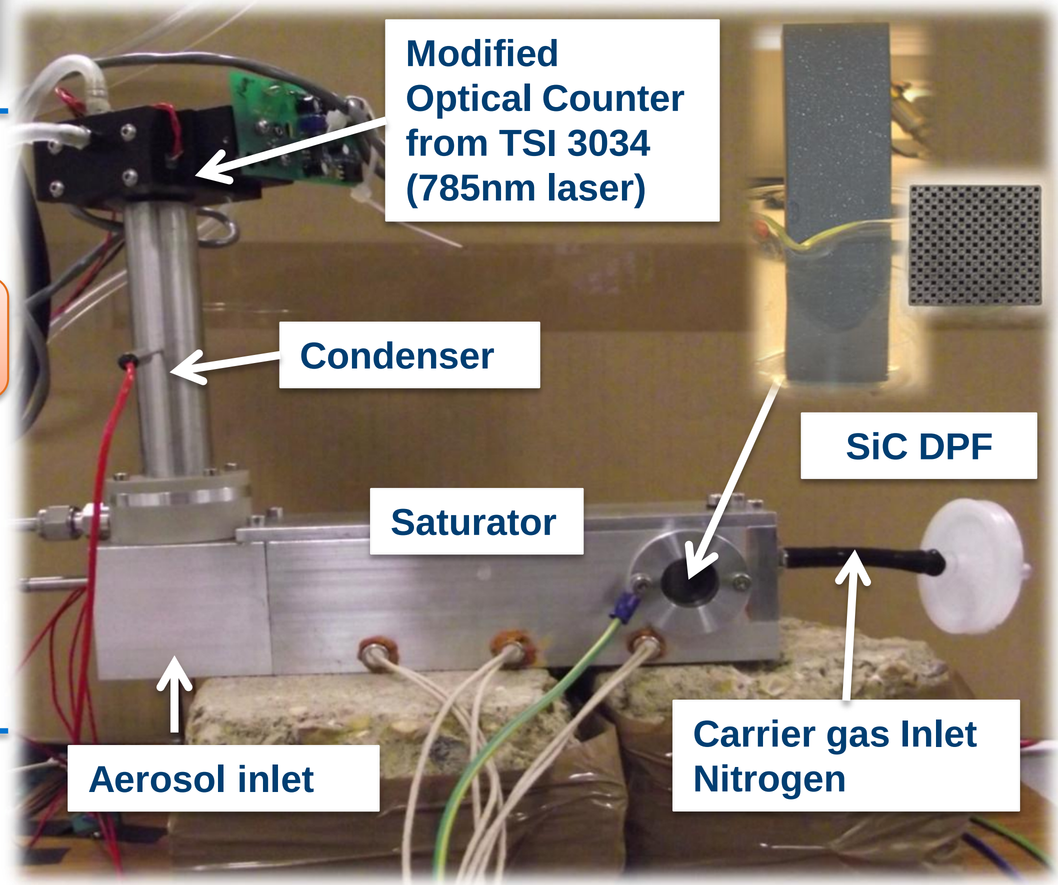
Pulse Counter Circuit

Software

PN concentration

Bubble Flowmeter

Temperature Controllers



Homogeneous nucleation

- Classical Theory of Homogeneous Nucleation is expressed in terms of bulk and surface contributions.
- The nucleation rate **$J = K \exp(-\Delta G^*/kT)$**

    - the formation free energy of critical clusters (ΔG^*)

    - the kinetic factor K = the impingement rate of vapour molecules onto the surface area of the critical cluster

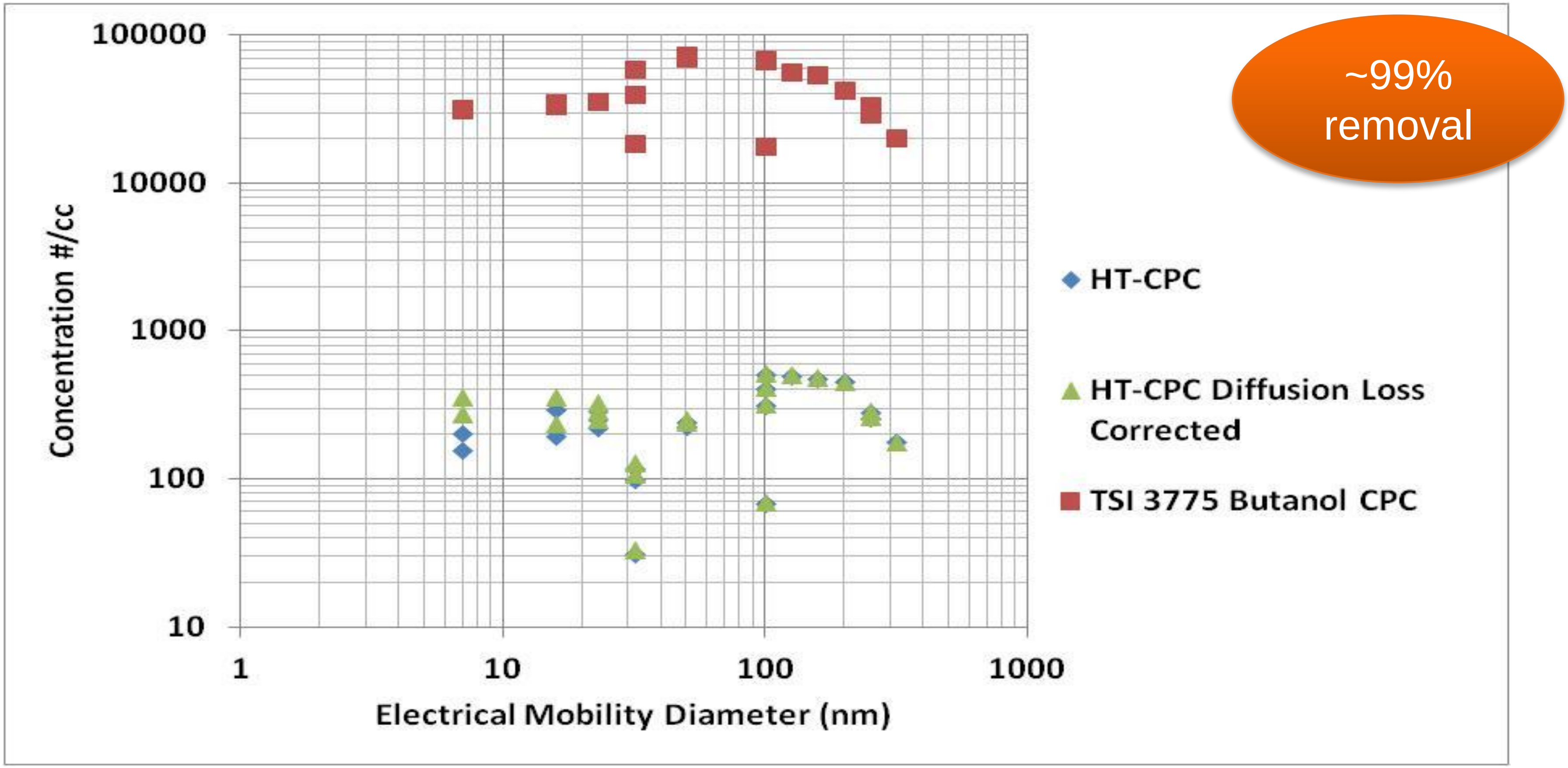
- Advantage of the Classical theory

    - we can use macroscopic properties of the species.

* Viisanen Y and Strey R (1994) Homogeneous Nucelation rates for n-butanol, J. Chem Phys 101 (9)

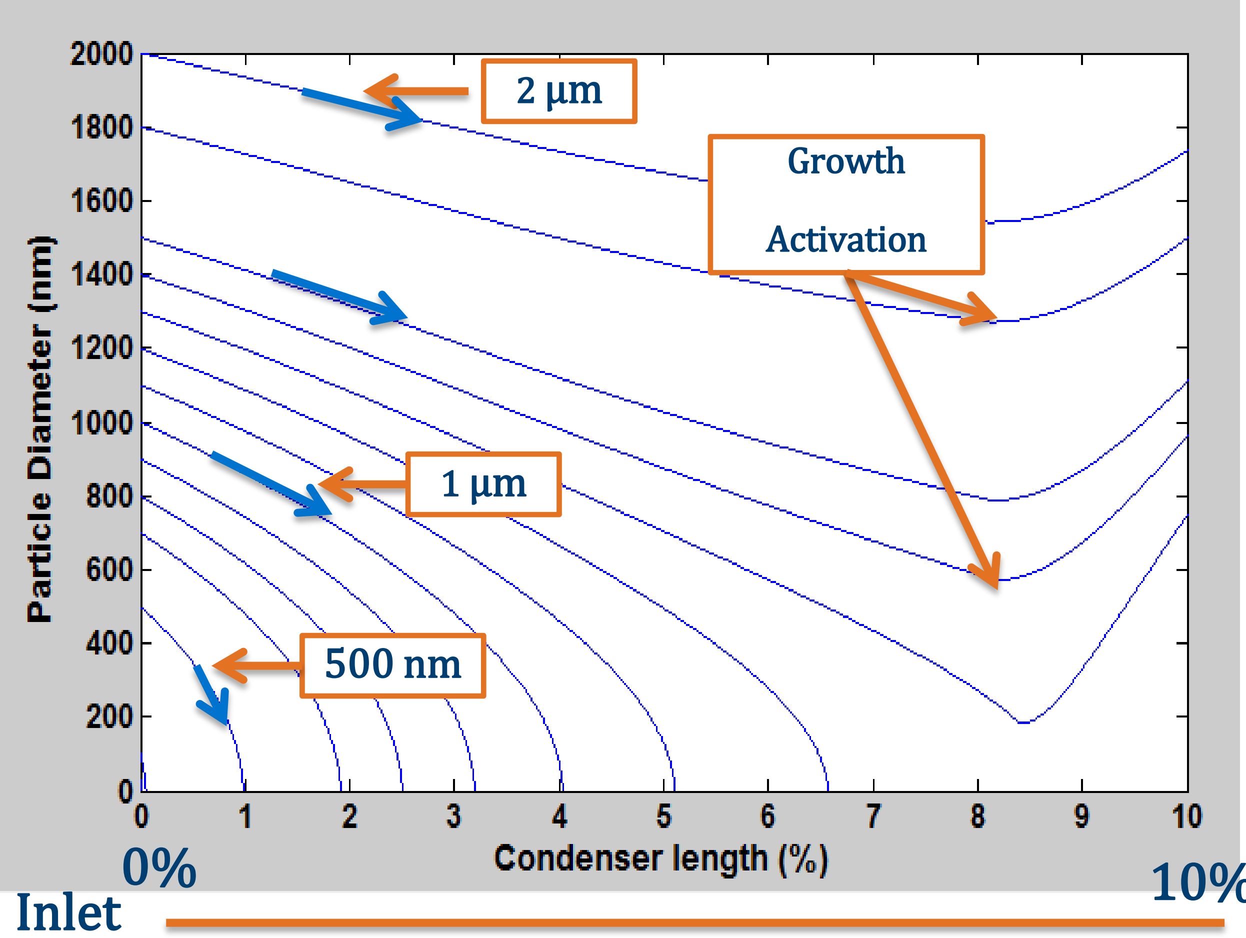
Experiment – Tetracontane Particles. Removal efficiency without sample pre-heating.

Tetracontane number concentration measured by the HT-CPC



Experiments – Tetracontane Removal Prediction

- Tetracontane Particle Diameter along condenser centreline



For Tetracontane ($C_{40}H_{82}$) particle concentration 10^4 #/cc

Simulation suggests small particles will evaporate completely but larger ones will be activated to grow.

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Experiments

- Lifetime comparison

Initial Diameter (nm)	Particle Lifetime (ms)		
	Ethanol @20°C	Water @20°C	Tetracontane @ High Temp CPC
10	0.0004*	0.002*	0.011
100	0.009*	0.030*	0.16
800	-	-	10

- Therefore, the prediction is physically reasonable.

* Hinds (1998), Aerosol Technology

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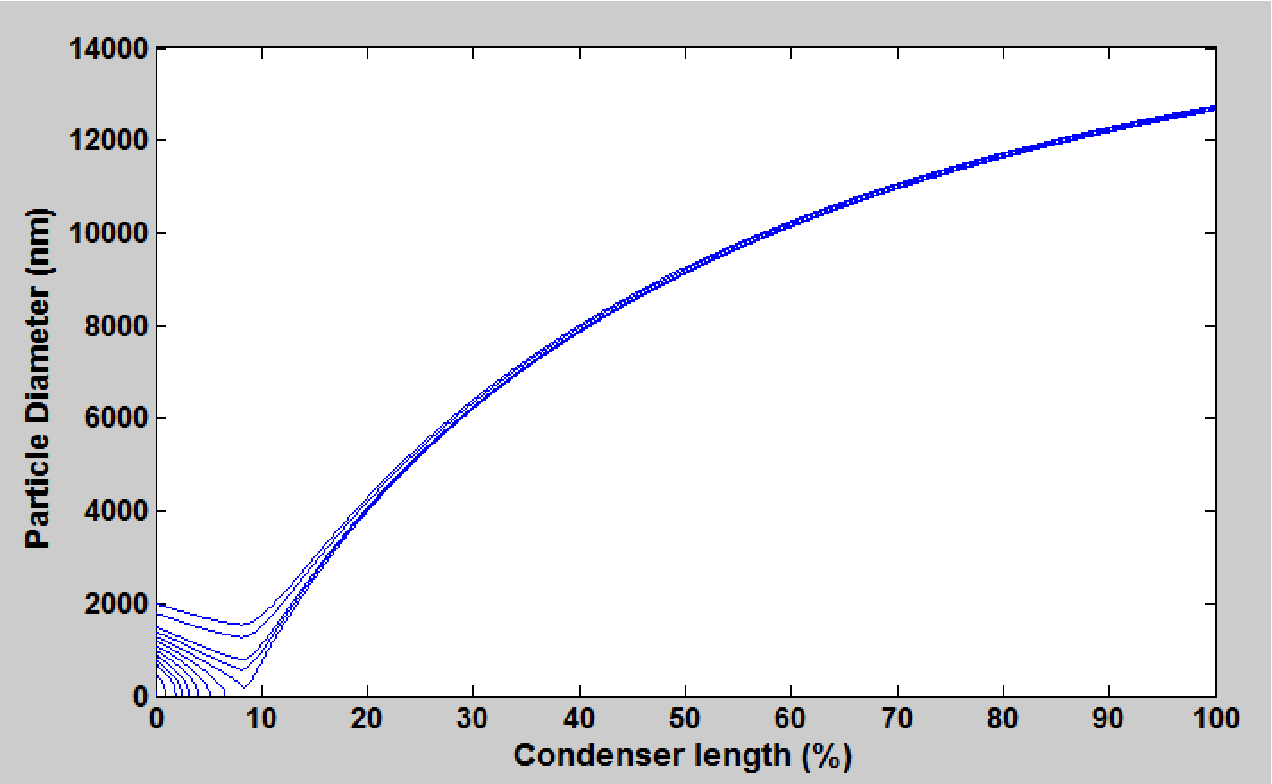
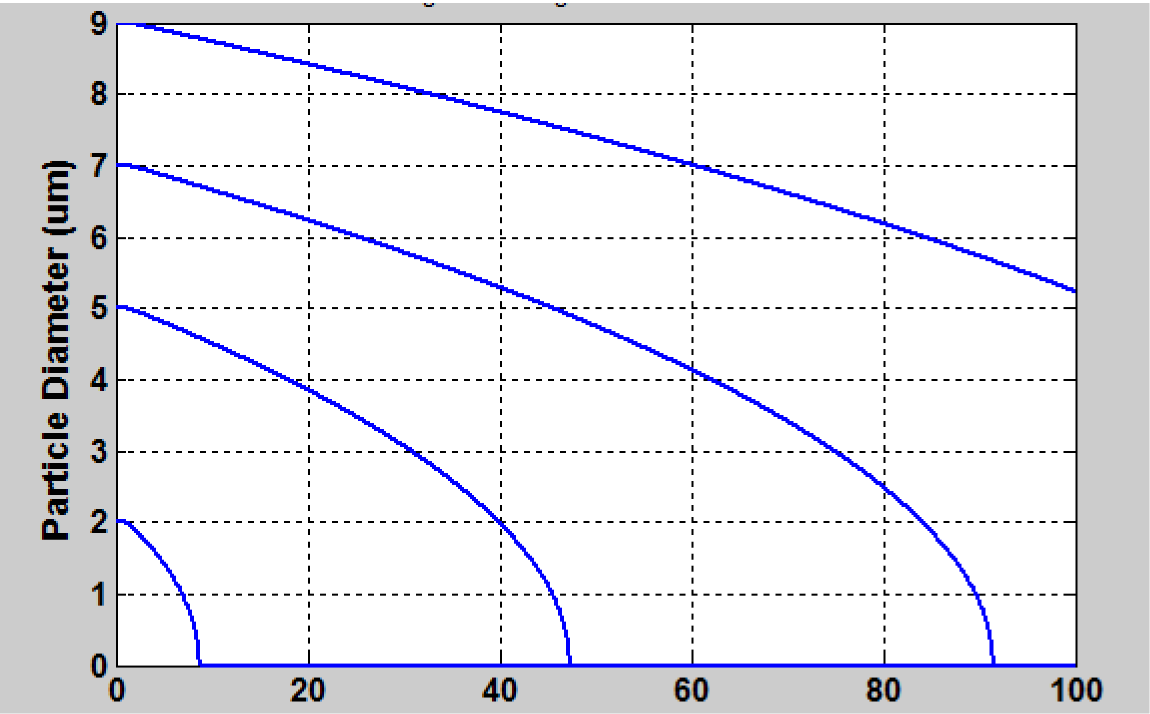
Tetracontane – evaporation in the HT-CPC

Tetracontane



Tetracontane – evaporation in sampling tube

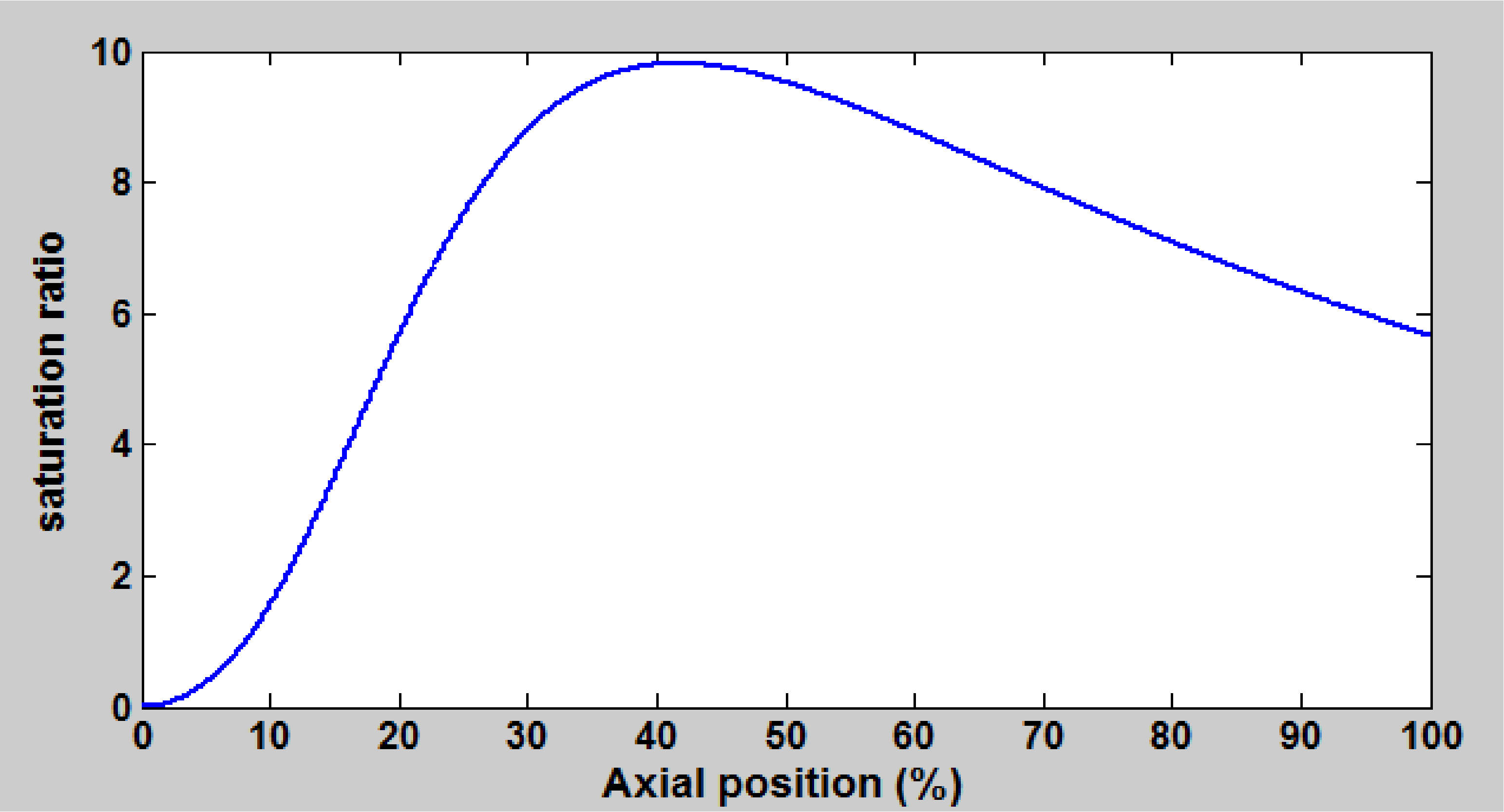
Tetracontane



Sampling tube length %
(L = 2 cm, diameter = 2 mm)

Saturation ratio in the condenser's centreline

For the HT-CPC running at the typical conditions 230/180℃



Butanol and DEHS properties

	Butanol	DEHS	Units
Tsat - Tcon	40 - 10	230 - 180	C
Operating Temperature (average Sat and Con)	25	205	C
Vapour Pressure at Topt	615.53	75.16	Pa
Vapour Pressure at Tsat	1769.7	277.71	Pa
Vapour Pressure at Tcon	181.0104	17.29	Pa
Air Thermal Diffusivity (α)	2.17E-05	5.04E-05	m2/s
Diffusivity in air (Dif)	8.70E-06	7.25E-06	m2/s
(Dif/α)	4.01E-01	1.44E-01	
Enthalpy of vaporisation	707290	110531	J/mol
density	805.85	784.3	kg/m3
Boiling point	117	377	C
surface tension	0.0239	0.0292	N/m