

Theoretical Investigation of Volatile Removal Efficiency of Particle Number Measurement Systems

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ABSTRACT

Euro 5/6 light-duty vehicle emissions regulation introduced non-volatile particle number emission measurements. The particle number measurement system consists of a volatile removal unit followed by a particle number counter with a 50% cut-point diameter at 23 nm. The volatile removal unit must achieve a >99% concentration reduction of a monodisperse aerosol of tetracontane ($\text{CH}_3(\text{CH}_2)_{38}\text{CH}_3$) particles of diameter ≥ 30 nm with inlet concentration $\geq 10^4 \text{ cm}^{-3}$.

In this paper the evaporation of tetracontane particles in the volatile removal unit is investigated theoretically. The temperature and the residence time in the evaporation tube are discussed, as well as the possibility of nucleation events of evaporated particles at the exit of the evaporation tube. In addition, sulfuric acid nucleation at the evaporation tube exit is analyzed. Theoretical calculations are, finally, compared to experimental data.

Our main conclusion is that the volatile removal efficiency requirements of the legislation can be easily met. However, as some experimental measurements showed, the removal efficiency might differ for large particle sizes and high concentrations; thus, the results of particle number counters with a 50% cut-point diameter less than 23 nm should be interpreted with care.

INTRODUCTION

The particle number measurement of non-volatile particles was introduced in the Euro 5/6 regulation [1, 2]. [Appendix B](#) presents a schematic diagram of the particle number system. Specifically, it consists of a volatile particle removal unit (VPR) and a particle number counter with a 50% cut-point (cut-off size) at 23 nm. The volatile removal unit consists of a

primary diluter where hot dilution occurs (sample temperatures reach $>150^\circ\text{C}$) and a heated tube with a wall temperature between 300 and 400°C . The heated tube (also referred to as evaporation tube) is used to evaporate volatile and semi-volatile particles that might be present in the sample or, at least, to reduce the volatile species present as nucleation mode particles to sizes <23 nm (via evaporation). The concept of the system and its volatile removal efficiency were discussed in [3].

According to the legislation, the volatile removal efficiency of the unit should be >99% for monodisperse tetracontane ($\text{CH}_3(\text{CH}_2)_{38}\text{CH}_3$) particles of diameters ≥ 30 nm with inlet concentration $\geq 10^4 \text{ cm}^{-3}$. As the sample is diluted at least 10 times in the primary diluter, concentrations $\geq 10^3 \text{ cm}^{-3}$ enter the heated tube. Many particle number systems were investigated experimentally in [4]. While all systems met legislation requirements, for higher concentrations or for tetracontane particles of larger diameters the requirements were not met, e.g., the removal efficiency was lower than required.

A major concern is how legislation requirements can be implemented in real-life applications. For light-duty vehicles there is no indication that the volatile nucleation mode cannot be efficiently removed: usually nucleation mode particles evaporate at temperatures below 130°C (e.g. [5]). However, during regeneration of Diesel Particulate Filters (DPFs) high concentrations of nucleation mode particles are generated. The combination of a VPR and a particle counter with a cut-off size at 23 nm did not measure these particles (e.g. [6]), an observation that doesn't necessarily mean that all nucleation mode particles had been completely removed. Furthermore, heavy-duty testing sometimes shows high particle concentrations at diameters <23 nm even downstream of the evaporation tube (e.g. [7]). These particles might be non-volatile or the inlet particles might not have evaporated

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completely in the evaporation tube (or they might have nucleated homogeneously at its exit). In the first case lowering the cut-off size of the particle number counter should be considered in the heavy-duty regulation, in the second case the volatile removal efficiency limitations of the systems should be recognized.

In this paper we investigate theoretically the evaporation of tetracontane particles in a heated tube at different temperatures for particles of different diameters and concentrations. Nucleation of evaporated particles and of sulfuric acid/water at the exit of the tube is also discussed. Finally, experimental data are presented and compared to theoretical calculations.

THEORETICAL BACKGROUND

EVAPORATION

The gas mean free path [8] is approximately given by:

$$\lambda = \lambda_r \left(\frac{101}{p_\infty} \right) \left(\frac{T}{293} \right) \left(\frac{1 + S_s / 293}{1 + 110/T} \right) \quad (1)$$

Where:

λ_r	m	Air mean free path at 293 K and atmospheric pressure (101 kPa) (= 66.4 nm).
T	K	Temperature
p_∞	kPa	Vapor ambient partial pressure
S_s	K	Sutherland constant (= 110 for air)

At temperature $t = 300^\circ\text{C}$ the air mean free path λ is 150 nm and at 150°C it is 105 nm. Note that we use the symbol T when the temperature is expressed in K and t when expressed in $^\circ\text{C}$. The symbol τ is used for time in s.

In the free molecular regime, when the particle diameter is less than the gas mean free path ($d_p < \lambda$), the rate of particle growth is governed by the rate of molecular collisions between the particle and the vapor molecules [9]. Accordingly, the following equation, derived from kinetic theory, is used to calculate the rate of particle shrinkage $d(d_p)/d\tau$ (m/s):

$$\frac{d(d_p)}{d\tau} = \frac{2Ma_c(p_\infty - p_d)}{\rho_p N_A \sqrt{2\pi n k_B T}} \quad d_p < \lambda \quad (2)$$

Where:

M	kg / mol	Molecular weight of the liquid (0.563 for tetracontane)
α_c	-	Condensation coefficient
p_d	kPa	Partial pressure at the droplet surface
ρ_p	kg / m ³	Density of (liquid) tetracontane particles
N_A	molec. / mol	Avogadro's number (6.022×10^{23})
m	kg / molec.	Mass of a vapor molecule ($= M / N_A$)
k_B	N m / K	Boltzmann's constant ($= 1.381 \times 10^{-23}$)

The condensation coefficient α_c is usually approximated to be 0.04; however, as we do evaporation and not condensation calculations we took it to be 1. Taking this coefficient to be 0.04 would lead to lower evaporation rates. The density and other required tetracontane properties may be found in [Appendix A](#).

The vapor ambient partial pressure may be expressed as:

$$p_\infty = p_s S \quad (3)$$

Where S is the saturation ratio and p_s the saturation pressure. The initial saturation ratio S was considered to be 0 (no vapor present when the particles enter the heated tube). The saturation ratio S after some time $d\tau$ was calculated from the following equation for p_∞ :

$$p_\infty = \frac{nRT}{V} \quad (4)$$

Where

R	J / mol K	Gas constant (= 8.314)
V	m ³	Volume (not needed)

The number of evaporated moles n is:

$$n = \frac{m_{p,tot}}{M} \quad (5)$$

Where the total tetracontane mass (in kg) in the vapor phase $m_{p,tot}$ is:

$$m_{p,tot} = C m_{evap} V \quad (6)$$

Where:

C particles / m³ Particle concentration
 m_{evap} kg / particle The mass of the tetracontane that has evaporated

$$m_{evap} = \rho_p \frac{\pi}{6} (d_{p1}^3 - d_{p2}^3) \quad (7)$$

Where subscripts 1 and 2 denote the initial and final particle diameter after a small time interval dt .

The partial pressure at the droplet surface is given by the Kelvin equation:

$$p_d = p_s \exp\left(\frac{4\gamma M}{\rho_p R T d_p}\right) \quad (8)$$

Where:

γ N / m Surface tension of the liquid droplet (Appendix A)

Note that in the free molecular regime the molecular condensation or evaporation rate depends on the available (geometric) surface area; consequently, the rate of change of the particle diameter depends on the particle diameter only through the Kelvin effect (Eq. (2)). Smaller particles evaporate faster as p_d is larger for smaller particles. However, our calculations show that for the same time the mass that evaporates is lower for smaller particles.

In the continuum regime, particle diameter larger than the air mean free path ($d_p > \lambda$), growth depends on the rate of diffusion of molecules to the droplet surface. The rate of particle growth for an isolated droplet of pure liquid is given by Eq. (9) [9], an equation that may also be used to calculate the evaporation rate:

$$\frac{d(d_p)}{d\tau} = \phi \frac{4D_v M}{R \rho_p d_p} \left(\frac{p_\infty}{T_\infty} - \frac{p_d}{T_d} \right) \quad d_p > \lambda \quad (9)$$

Where:

D_v m² / s Diffusion coefficient of a condensing vapor molecule
 ϕ - Fuchs correction factor (or Knudsen correction)

$$\phi = \frac{2\lambda + d_p}{d_p + 5.33(\lambda^2 / d_p) + 3.42\lambda} \quad (10)$$

The droplet temperature T_d may be estimated by balancing the latent heat released to the droplet due to condensation to the heat lost by conduction to the cooler surrounding air. At steady state

$$T_\infty - T_d = \frac{D_v M H}{R k_v} \left(\frac{p_d}{T_d} - \frac{p_\infty}{T_\infty} \right) \quad (11)$$

Where

H kJ / mol Latent heat of evaporation
 k_v W / m K Thermal conductivity of the gas (air) (Appendix A)

For the temperature range examined here (0-300°C) the droplet temperature change was negligible; thus, we approximate $T_d = T_\infty$.

Note that in the continuum regime the rate of change of the particle diameter (growth, shrinkage) is inversely proportional to the particle diameter (Eq. (9)). Smaller particles evaporate faster, but our calculations show that for the same time the mass that evaporates is lower for smaller particles.

As legislation for the volatile removal efficiency defines a diameter for the test aerosol all results will be presented in terms of particle (droplet) diameter.

NUCLEATION

At the evaporation tube outlet volatile particles have evaporated. As the tetracontane vapor exits the tube it cools to ambient temperature, a process that may induce homogeneous nucleation to reform particles. This was checked by calculating the homogeneous nucleation rate J (cm⁻³ s⁻¹) as given by Classical Nucleation Theory [10]:

$$J = \left(\frac{2\gamma}{\pi n} \right)^{1/2} \frac{v N^2}{S} \exp\left(\frac{-i^* \ln S}{2} \right) \quad (12)$$

$$i^* = \frac{32\pi}{3} \frac{v^2 \gamma^3}{(kT)^3 (\ln S)^3} \quad (13)$$

Where

v	$\text{cm}^3 / \text{molecule}$	Molar volume ($= M / \rho_p / N_A$)
N	monomers / cm^3	Number concentration of monomers ($= p_\infty / k_B / T$)

The vapor saturation ratio S is given by Eq. (3). The ambient partial pressure p_∞ (Eq. (4), (5), (6), (7)) of fully evaporated tetracontane particles, which had entered the tube with inlet number concentration C , was determined by requiring that it generates a nucleation rate $J = 1 \text{ cm}^{-3} \text{ s}^{-1}$.

The same equations were also used to calculate single-component H_2SO_4 nucleation. However, since H_2SO_4 nucleates easier in the presence of H_2O , an empirical equation [10] was used to determine the critical concentration C_{crit} ($\mu\text{g}/\text{m}^3$) of gas-phase sulfuric acid that produces a binary H_2SO_4 - H_2O nucleation rate of $J = 1 \text{ cm}^{-3} \text{ s}^{-1}$. The equation is:

$$C_{crit} = 0.16 \exp(0.1T - 3.5RH - 27.7) \quad (14)$$

Where RH is the relative humidity (varying from 0 to 1).

RESULTS

EVAPORATION

Figure 1 shows the particle diameter decrease (due to evaporation) of tetracontane particles for different initial diameters and temperatures. For 30 nm particles Eq. (2) was used, for 200 nm particles Eq. (9), whereas for 100 nm particles both equations were used. A residence time of 0.3 s was considered to be characteristic of residence times in evaporation tubes or thermodesorbers (thermodenuders) (e.g. 0.3 s in the Dekati thermodenuder, 0.2 s in the evaporation tube of the Matter Eng. particle number system, 0.5 s in the evaporation tube of the AVL particle number system). The air mean free path λ is also shown. The results show that a wall temperature of 150°C is necessary to evaporate the tetracontane particles in less than 0.3 s. We consider that the aerosol temperature equal the wall temperature. Note that Eq. (2) with condensation coefficient of 0.04 instead of 1 would give temperatures approximately 50°C higher. Note also that the predictions of the two equations (2) and (9) differ by about 50°C at the transition regime, i.e., when the particle diameter is comparable to the air mean free path. This discontinuity arises because the free molecular limit of ϕ is 1.2 times the value of Eq. (2) [11]. The results shown in Fig. 1 are in good agreement with experimental results for 30 and 70 nm dotriacontane ($\text{CH}_3(\text{CH}_2)_{30}\text{CH}_3$) particles that evaporated completely at temperatures 110 and 140°C, respectively [12].

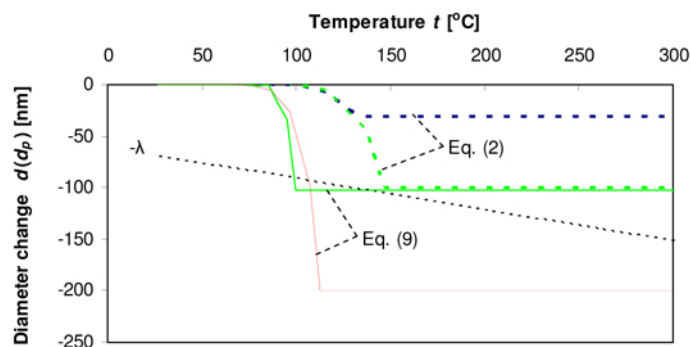


Figure 1. Diameter change of 30 nm (blue), 100 nm (green) and 200 nm (red) tetracontane particles in an evaporation tube with different wall temperatures (residence time 0.3s).

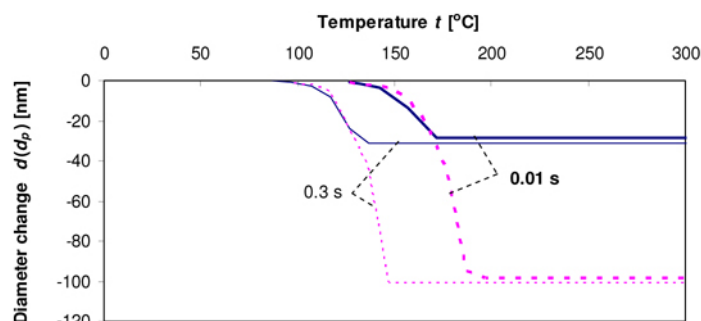


Figure 2. Diameter change of 30 nm (blue) and 100 nm (red) tetracontane particles in an evaporation tube with different wall temperatures and residence times. Equation (2) was used.

The effect of the residence time is shown in Figure 2. The calculations show that even a short residence time of 0.01 s (all commercial evaporation tubes should have residence times larger than 0.01 s) is adequate to evaporate the tetracontane particles. However, for the short residence time the minimum wall temperature required is 50°C higher (200°C).

Figures 1 and 2 refer to low evaporation tube inlet particle number concentrations (of the order of 10^4 cm^{-3}). For high inlet concentrations the evaporated tetracontane (vapor) mass increases changing significantly the saturation ratio S , thereby affecting the evaporation rate. Figure 3 shows the inlet concentrations that lead to incomplete evaporation of tetracontane particles of different diameters at 200°C. This wall temperature was chosen because at higher temperatures (e.g., 300°C) tetracontane particles are predicted to evaporate completely even at very high concentrations, whereas at lower temperatures (e.g., 150°C) the particles are predicted not to evaporate within 0.3 s, even at extremely low concentrations. The calculations show that inlet concentrations that evaporate completely, even at 200°C, are very high. Therefore, for all practical applications where