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compounds on  
nanoparticle  
formation**

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# Effect of organic compounds on nanoparticle formation in diluted diesel exhaust

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Received: 6 November 2003 – Accepted: 8 January 2004 – Published: 15 January 2004

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## Abstract

The nucleation of nanoparticles in the exhaust of a modern light-duty diesel vehicle was investigated on a chassis dynamometer. This laboratory study is focused on the influence of volatile organic compounds (VOCs) on nucleation of volatile nanoparticles. Different organic compounds were added to the dilution air of the particle sampling under different sampling conditions. Sample temperature and relative sample humidity were varied in a wide range. The number size distribution of the particles was measured with a scanning mobility particle sizer (SMPS) and showed significant differences in response to the added organic compounds. While the nucleation mode particles showed a large variation in concentration, the accumulation mode particles remained unchanged for all compounds. Depending on the functional group, organic compounds were capable of initiating and increasing (alcohols and toluene) or decreasing (acetone, aniline, and methyl tert-butyl ether (MTBE)) nucleation mode particles. Short volatile aliphatic hydrocarbons (hexane and cyclohexane) turned out to be without effect on nucleation of nanoparticles. Possible reasons for the differences are discussed.

## 1. Introduction

Exhaust from diesel engines represents an important anthropogenic source of particles in ambient air. Particles from internal combustion engines can be divided into solid and volatile particles (Kittelson, 1998). The solid particles mainly consist of agglomerated carbonaceous primary particles, which are usually described as soot. However, other compounds such as hydrocarbons can be adsorbed or condensed on its surface. The volatile nanoparticles are usually formed by nucleation of sulfuric acid, water, and other species. Formation of these volatile nanoparticles strongly depends on the dilution and cooling process of the exhaust. The two different kinds of particles usually form separate modes in the number size distribution, that are referred to as “accumulation mode” and “nucleation mode”.

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Adverse health effects of particles on human health have been documented in several studies (Pope, 2000; Petrovic et al., 2000; Oberdörster, 2001). Impact on health has mainly been studied for soot particles and thus, there is limited information about volatile nanoparticles. Because volatile nanoparticles have a distinctly smaller diameter than soot particles, the mass contribution of volatile nanoparticles is usually small. However, investigations has documented that health effects were more related to particle number than to mass (Donaldson et al., 1998; Sydbom et al., 2001) even though the current legislation for particle emissions is based on mass. Compared to soot a higher deposition rate in the lungs might be expected for volatile nanoparticles because of their smaller diameters. As indicated in a study by Kim and Jaques (2000), the deposition rate of 40 nm solid nanoparticles is nearly 2.5 times higher than for 100 nm nanoparticles. To assess the human health impact of volatile nanoparticles, more information about their exact composition is needed. Sulfuric acid seems to be a relevant compound for human health effects in volatile nanoparticles. Inhalation of acid aerosols in laboratory animal studies causes genotoxic damage in cells (Soskolne et al., 1984; Swenberg and Beauchamp, 1997). Kilgour et al. (2002) showed cell proliferation of the respiratory tract in rats due to exposure to sulfuric acid.

Improvements in engine technologies have reduced particle mass emissions from diesel engines. The limit values for mass emissions from light-duty diesel vehicles were gradually reduced by more than four times from  $0.18 \text{ g km}^{-1}$  (Euro 1, since 1992) to  $0.025 \text{ g km}^{-1}$  (Euro 4, as of 2005). A reduction in mass is related to a decrease in number of soot particles, but there is no clear relation to the volatile nanoparticle emissions (Mohr et al., 2001). It is generally accepted that volatile nanoparticles are influenced by dilution parameters such as temperature, dilution ratio, residence time, and humidity (Abdul-Khalek et al., 1999; Khalek et al., 2000; Mathis, 2002). In addition, the fuel sulfur content plays an important role (Ntziachristos et al., 2000; Maricq et al., 2002). Volatile nanoparticles are observed in both laboratory and chasing experiments, but the observed nucleation mode in chasing studies could not have been reproduced in laboratory control experiments yet (Kittelson, 2002; Vogt et al., 2003). A

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possible explanation could be the high sensitivity of the nucleation mode to the dilution parameters. Kittelson (1998) reported that a dilution ratio of 1000 is typical for an atmospheric dilution process of exhaust. However, such a high dilution ratio cannot be applied for many laboratory studies due to the high requirements of the dilution ratio control. Nevertheless, laboratory studies facilitate a better principle understanding of the formation process of volatile nanoparticles.

If the concentration of soot particles is sufficiently large, volatile nanoparticles can be quenched. Moreover, pre-existing soot particles scavenge a part of the volatile nanoparticles by collision (Seinfeld and Pandis, 1998). As the total surface provided by soot particles is reduced, the relevant species responsible for nucleation remain in the gaseous phase and can lead to homogeneous nucleation (Kittelson, 1998; Mohr et al., 2001). However, the classical binary nucleation theory of water and sulfuric acid underestimates the formation of nucleation mode particles by several orders in number and thus, further species are suspected to be involved in nucleation (Shi and Harrison, 1999; Khalek et al., 2000). Besides the explanation of classical binary homogeneous nucleation of sulfuric acid and water in diesel exhaust, homogeneous ternary nucleation of sulfuric acid, ammonia, and water (Napari et al., 2002) or nanoparticle formation from chemiions generated during combustion (Yu, 2001; Yu, 2002) were reported. Organic compounds are often considered as the key species to control the growth of nucleation mode particles (Maricq et al., 1999; Kerminen et al., 2000; Khalek et al., 2000; Zhang and Wexler, 2002). Analytical investigations of the volatile nanoparticles in diesel exhaust has given strong indications that organic compounds were involved in the nucleation process (Tobias et al., 2001; Sakurai et al., 2003). The role of organic compounds has been investigated in more detail for the formation of cloud condensation nuclei (CCN) than for the dilution process of engine exhaust. The organic compounds found in CCN are mainly organic acids such as formic, acetic, pyruvic, pinonic oxalic, and malonic acids (Yu, 2000; Hegg et al., 2001; Giebl et al., 2002). Little is known about organics with other functional groups. We investigated how non-acid organic compounds are involved in the nucleation process of volatile particles in diluted

diesel exhaust. We added a variety of VOCs (aliphatic hydrocarbons, aromatic compounds, a ketone, an amine, an ether, and alcohols) into the primary dilution air. The intention of this laboratory study is to contribute to a better understanding of organic compounds that are involved in the nucleation process of diluted diesel exhaust.

## 2. Experimental

### 2.1. Vehicle and fuel

All experiments were conducted with a modern light-duty diesel vehicle on a chassis dynamometer at constant speed ( $50 \text{ km h}^{-1}$ ) and increased load conditions ( $7.0 \pm 0.2 \text{ kW}$ ,  $18.1 \pm 0.5\%$  of maximum power, 2100 rpm). The normal load was 2 kW under road conditions. The engine parameters and the results of fuel analysis are listed in Tables 1 and 2. The tests were run with a standard fuel with a sulfur concentration of 323 ppm. The additional sulfur contribution in the exhaust by lube oil consumption was estimated to be 6 ppm. The vehicle was running at  $7.0 \pm 0.2 \text{ kW}$  load for at least 20 min to conditionate the vehicle and sampling system.

### 2.2. Sampling

The overall set-up of the particle measurement is shown in Fig. 1. The relevant nucleation parameters such as dilution ratio, dilution temperature, and residence time were kept constant. Dilution of the exhaust sample was performed with a two-stage dilution unit. The primary dilution of the exhaust was accomplished inside a porous tube (Dekati prototype), which was inserted directly into the tailpipe to minimize sampling losses. Detailed information about the diluter can be found in Mikkanen et al. (2001). By controlling the temperature of the dilution air by means of a vortex cooler, the sample temperatures ( $T$ ) were in the range of  $34.7 \pm 0.5^\circ\text{C}$  or  $44.5 \pm 0.5^\circ\text{C}$ , respectively. The sample temperature was measured immediately after the first dilution. The dilution ratio

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was set to  $8.5 \pm 0.5$  by the flow ratio of the dilution air to the raw exhaust. Downstream of the first dilution stage unit, a residence chamber was inserted offering sufficient time for the relevant nucleation compounds to nucleate. A constant residence time of  $2.50 \pm 0.15$  s was chosen. The second dilution unit was placed at the end of the residence chamber to quench the formation and growth of nucleation mode particles. The dilution ratio of this ejector dilution unit remained constant at 10.

To vary humidity in the exhaust sample, a part of the dilution air of the primary diluter was bubbled through a flask filled with de-ionized water before entering the porous tube diluter. Relative humidity of the dilution air ranged from 4% to 75% at ambient temperature, measured by a humidity sensor (Rotronic BM90). Further contributions to the humidity came from combustion of the diesel fuel and the combustion air. Calculation of the combustion air humidity was based on a typical diesel fuel elemental composition of 14% hydrogen and 86% carbon. The combustion air was measured to be 50% relative humidity at 25°C and 950 hPa. Taking all contributions into account, the relative sample humidity after the first dilution unit was calculated to range from 30% to 99% at the measured sample temperature. The relative sample humidity is hereafter referred to as humidity (*RH*). To adjust the gas concentration of the selected organic compounds in the sample, the pure organic compounds were filled into an additional flask as shown in Fig. 1. Some of the liquid organic compounds filled in the flask could uptake water from the dilution air and reduce the relative humidity of the dilution air. This effect was considered to be negligible in this study. All added organic compounds were of technical quality (Fluka). Control experiments by evaporating the organic compounds and de-ionized water in the flask showed no particle formation: The dilution air enriched with the organic compounds and water was analyzed by a scanning mobility particle sizer (SMPS, TSI) without observing any particles in the number size distribution. Concentrations of the organic compounds added to the exhaust were measured with a flame ionization detector (FID, Horiba Mexa-7400H) after the first dilution and were normalized to the effective number of carbon. The FID was calibrated with propane in the linear region from 1 ppm to 5000 ppm corrected as

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$C_1$ . When the concentration exceeded the concentration of 5000 ppm corrected as  $C_1$ , we present the data as larger than the highest measured concentration corrected for the added organic compound (e.g. >5600 ppm toluene in Fig. 6, top panel).

### 2.3. Particle number size distribution

5 A SMPS consisting of a differential mobility analyzer (DMA, TSI 3071) and a condensation particle counter (CPC, TSI 3025) was used for determining the number size distribution of the particle. The DMA had a polydisperse inlet flow of  $1.5 \text{ l min}^{-1}$  and a sheath air flow of  $15 \text{ l min}^{-1}$  that selected particle diameters ranged from 7 nm to 214 nm. The impactor upstream of the DMA was removed because the pressure drop  
10 was too high to properly operate the CPC. A bypass to the DMA ( $4.8 \text{ l min}^{-1}$ ) was installed to increase the flow rate and reduce diffusion losses. Therefore, no correction of diffusion losses was conducted.

### 2.4. Calculation of the organic vapor concentration

Based on the FID measurements, the vapor pressure  $p_i$  of the substance  $i$  in the  
15 sample air was calculated according to the ideal gas equation:

$$p_i = \frac{(C_{\text{ppm}} - C_{\text{background}}) \cdot 10^{-6}}{M_v} R \cdot T, \quad (1)$$

where  $R$  is the universal gas constant ( $8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$ ),  $T$  is the absolute temperature,  $C_{\text{ppm}}$  is the volume concentration in ppm of the substance  $i$ ,  $C_{\text{background, ppm}}$  is the concentration without adding any VOCs, and  $M_v$  is the mole volume.  $C_{\text{background, ppm}}$  was  
20 measured experimentally to be 5 ppm for all measurements.

The vapor pressure  $P_{S_i}$  in Torr over the pure liquid phase for a flat surface was calculated for the substance  $i$  according to the Antoine equation (Lange and Dean,

1973):

$$\log_{10} P_{Si} = A - \frac{B}{C + t}, \quad (2)$$

or alternatively, for 1-butanol with

$$\log_{10} P_{Si} = C - \frac{52.23 \cdot B}{(t + 273.15)}, \quad (3)$$

5 where  $A, B,$  and  $C$  are constants and  $t$  is the temperature in  $^{\circ}\text{C}$ .

The constants  $A, B,$  and  $C$  were taken from Lange and Dean (1973). For 1-hexanol and MTBE the values were taken from Poling et al. (2001) and Krähenbühl and Gmehling (1994), respectively.

10 To compare the vapor pressures with each other, a common quantity was introduced. A good approach is the saturation ratio  $S_i$ ; the ratio of the partial vapor pressure  $p_i$  to the saturation vapor over the pure liquid phase  $P_{Si}$ :

$$S_i = \frac{p_i}{P_{Si}}. \quad (4)$$

### 3. Results and discussions

15 The aim of this investigation was to study a selection of VOCs on the nucleation process at varying temperature and humidity of the sample. Because the nucleation process reacts very sensitively to small changes of the dilution conditions, it had to be verified that the increase of humidity and VOCs in the dilution air did not influence any sampling parameters. Regarding the key parameters listed in Table 3, the variations of the sampling parameters are small within a test series. The variations from one test to another  
20 mainly depended on the restart of the vehicle. To unambiguously assign the effect of VOCs, the influence of the other key parameters were recorded. A typical temperature variation of the dilution flow, sample flow, and exhaust flow within the same test series

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is shown for 2-propanol in Fig. 2. Variations of temperatures were randomly distributed and were not dependent on the concentration of 2-propanol in the dilution air. Based on these control experiments, it was verified that an increase of humidity and VOCs did not influence the sampling parameters.

The variation of the accumulation mode was found to vary  $\pm 25\%$  from one test series to another when the vehicle was restarted. A possible reason could be the corresponding vehicle load variation of  $\pm 3\%$  at this very sensitive operation point. In line with the load variation the exhaust temperature varied  $\pm 6^\circ\text{C}$  (see Fig. 2). Nevertheless, the load could be set within  $\pm 1\%$  for a test series that provided stable test conditions without any significant effect on the accumulation mode particles.

To investigate at which step of nucleation VOCs have an impact, three test conditions A, B, and C were evaluated. The key nucleation parameters of these three conditions are presented in Table 3. Tests without any addition of VOC revealed the following results: Under test condition A (sample temperature ( $T$ )= $44.9^\circ\text{C}$ , relative humidity ( $RH$ )= $36.3\%$ ) no or only a weak nucleation mode could be detected. Under condition B ( $T=44.3^\circ\text{C}$ ,  $RH=81.2\%$ ) a nucleation was always observed, which is explained by the higher humidity compared to condition A ( $T=44.9^\circ\text{C}$ ,  $RH=36.3\%$ ). The strongest nucleation occurred under condition C ( $T=34.7^\circ\text{C}$ ,  $RH=31.6\%$ ) as the low dilution air temperature provoked nucleation already at low humidity levels.

### 3.1. Effect of humidity

To distinguish the effect of humidity and VOCs in the dilution air on the nucleation process, a first series was conducted varying only the humidity in the dilution air. The sample temperature was either held at  $45.0^\circ\text{C}$  or at  $34.2^\circ\text{C}$ . Figure 3 depicts the effect of humidity on nucleation under both conditions. A considerable humidity effect on the nucleation mode particles was found at a sample temperature of  $45.0^\circ\text{C}$ . When the humidity was increased, a strong rise of the nucleation mode particles was observed. In addition, this peak moved to slightly higher diameters with increasing humidity. This can be explained by stronger coagulation due to a higher concentration

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of volatile nanoparticles at 99% relative humidity. The accumulation mode remained stable at about 70 nm. There was a distinct nucleation mode under dry conditions at 31% relative humidity and a sample temperature of 34.2°C. The nucleation mode particles increased by a factor of two when the relative humidity was increased from 31% to 81%. In comparison with the sample temperature at 45.0°C, there was a considerably lower influence of humidity on the nucleation process. To compare the strength of nucleation, the ratio of the maximum number concentrations in the nucleation mode to the accumulation mode was calculated. Due to this normalization, no correction of the particle number size distribution by the dilution ratio was necessary. This ratio is presented as a function of the relative humidity in the sample in Fig. 4. Below about 60% relative humidity, no appreciable nucleation took place at a sample temperature of 45.0°C indicating a minimal initial relative humidity for nucleation. As soon as the relative humidity was further increased, a clear dependence on humidity was observed. The ratio of the maximum number concentrations of nucleation mode to the accumulation mode showed a linear dependence on the humidity over the entire investigated range at a sample temperature of 34.2°C. The lower sensitivity on humidity at a sample temperature of 34.2°C is apparent when the slope is compared under the assumption of linear response. The sample temperature at 45.0°C with a slope of 0.062 (% relative humidity)<sup>-1</sup> had a significantly steeper slope than at 34.2°C with a slope of 0.037 (% relative humidity)<sup>-1</sup>. In spite of the bigger humidity effect on the volatile nanoparticles at a sample temperature of 45.0°C, the absolute concentration of volatile nanoparticles was always higher at 34.2°C. Our experimental work is in accordance with the parametric study of Kim et al. (2002). A linear dependence was found of the nucleation rate as a function of relative humidity under conditions of increased humidity.

### 3.2. Effect of organic vapors on the nucleation mode

To find out which substance classes affect the nucleation process, a variety of organic compounds were added. The measured hydrocarbon concentration corrected as C<sub>1</sub> ranged from 500 ppm to 5000 ppm in the mixed sample part and exceeded the

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normal concentrations in exhaust gas by one or two orders of magnitude. However, concentrations of several thousands ppm are typical for cold starts at low temperatures. We found raw gas concentrations of 5000 ppm to 20 000 ppm and 10 000 ppm to 30 000 ppm for diesel and gasoline vehicles, respectively, in the first minutes of cold starts at  $-20^{\circ}\text{C}$ . Since we operated the engine at warm conditions, the oxidation catalyst converted hydrocarbons to a large extent. However, we do not intend to simulate the real world situation at this engine operation point but to gain a principle understanding of the nucleation process in presence of organic compounds. The added chemical compounds consisted of aliphatic hydrocarbons, aromatic compounds, a ketone, an amine, an ether, and alcohols. The chemical structures of these compounds are shown in Table 4. We chose compounds of high volatility to prevent losses by condensation on the sampling system. We are aware that less volatile organic compounds are more likely to be involved in the nucleation process under atmospheric conditions. Sakurai et al. (2003) reported that organic compounds from diesel nanoparticle was comprised of medium molecular weight with carbon numbers in the range from  $\text{C}_{24}$  to  $\text{C}_{32}$  for aliphatic hydrocarbons. However, our objective of this laboratory study was to identify the functional groups that are involved in the nucleation process. Therefore, the volatility of the organic compounds only played a minor relevance for the interpretation of our data.

An overview of the effect of the organic compounds on the nucleation mode is given in Fig. 5. To compare the strength of nucleation, the ratio of the maximum number concentrations in the nucleation mode to the accumulation mode was calculated.

### 3.2.1. Aliphatic hydrocarbons

The effect on nucleation mode particles was investigated for two aliphatic hydrocarbons, hexane and cyclohexane. For both compounds, no effect was observed on the particles in the nucleation mode though the concentration in the dilution air was increased up to 8000 ppm (see Fig. 5). However, due to their high volatility the saturation ratio remained always below 0.41%. Besides the low saturation ratio, little interaction

of these hydrophobic molecules with the main nucleation mode particles (water and sulfuric acid) exists.

### 3.2.2. Aromatic compounds

Toluene was chosen due to its high volatility compared to other polyaromatic compounds. Toluene influenced the nucleation mode particles under all conditions investigated, but only at the highest toluene concentration. Similar to the effect of humidity, the nucleation process was more affected when no or a weak nucleation mode existed in the beginning as under conditions A ( $T=44.9^{\circ}\text{C}$ ,  $RH=36.3\%$ ) and B ( $T=44.3^{\circ}\text{C}$ ,  $RH=81.2\%$ ) than for a strong nucleation mode as under condition C ( $T=34.7^{\circ}\text{C}$ ,  $RH=31.6\%$ ). Interestingly, toluene was capable of triggering a nucleation mode under condition A ( $T=44.9^{\circ}\text{C}$ ,  $RH=36.3\%$ ) when no spontaneous nucleation occurred (see Fig. 6, top panel). Obviously, the hydrophobic toluene associates with the nucleation mode particles. Following a suggestion by Tobias et al. (2001), a two-phase system of the hydrophobic compounds and water/sulfuric acid is proposed because it is unlikely that an association takes place between toluene and water/sulfuric acid. It likely seems that the organic phase was mainly created by the added toluene. Compared to other factors affecting the nucleation process, e.g. humidity, the increased nucleation mode particles due to the addition of toluene were moderate. Therefore, hydrophobic compounds with vapor pressures comparable to or higher than toluene (38 hPa at  $25^{\circ}\text{C}$ ) are assumed to be irrelevant for the nucleation process in diluted diesel exhaust.

For aniline, a further increase of nucleation mode particles is expected because hydrogen bonds to water and sulfuric acid can be formed providing additional stabilization. Nucleation mode particles were not influenced under conditions A ( $T=44.9^{\circ}\text{C}$ ,  $RH=36.3\%$ ) and C ( $T=34.7^{\circ}\text{C}$ ,  $RH=31.6\%$ ). The only effect appeared under condition B ( $T=44.3^{\circ}\text{C}$ ,  $RH=81.2\%$ ; see Fig. 6, bottom panel). Instead of the expected increase of nucleation mode particles with additional aniline, a weak reduction was observed. A possible explanation could be the reaction of the basic amino group of the aniline

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with the sulfuric acid and thus, formation of anilinium sulfate particles. This process removes sulfuric acid from the exhaust air resulting in a lower sulfuric acid vapor concentration and a decrease in nucleation. However, no relevant change of the particle number size distribution was observed indicating the existence of anilinium sulfate particles. We assume in the following that the reduction of nucleation is completely caused by an acid-base reaction of sulfuric acid with aniline creating particles in the size range of accumulation mode particles. The volume of the nucleation mode particles with a diameter  $< 30$  nm was calculated for the data shown in Fig. 6 (bottom panel, at the lowest and highest aniline concentration) and compared with the volume of the particles with a diameter  $> 30$  nm. The volume of particles with a diameter  $< 30$  nm contributed less than 2% to the volume of the particles with a diameter  $> 30$  nm. Therefore, no significant change of the particle number size distribution would be expected if anilinium sulfate particles had been formed.

### 3.2.3. Acetone

Acetone was chosen due to its high volatility. Without pre-existing nucleation mode particles, under condition A ( $T=44.9^{\circ}\text{C}$ ,  $RH=36.3\%$ ), no effect on the nucleation was detected with addition of the compound. The effect of acetone was relatively weak and consisted in a decrease of nucleation mode particles with increasing acetone concentration in the sample under condition B ( $T=44.3^{\circ}\text{C}$ ,  $RH=81.2\%$ ) and C ( $T=34.7^{\circ}\text{C}$ ,  $RH=31.6\%$ ). As an example, condition C ( $T=34.7^{\circ}\text{C}$ ,  $RH=31.6\%$ ) is depicted in Fig. 10.

### 3.2.4. MTBE

Due to its high relevance as a gasoline additive, MTBE was chosen. MTBE leads to more complete combustion due to the oxygen contained in the molecule (Poulopoulos and Philippopoulos, 2003). The nucleation mode particles showed a strong decrease as soon as the MTBE concentration was increased. Similar to acetone,

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no nucleation mode particles occurred with addition of MTBE under condition A ( $T=44.9^{\circ}\text{C}$ ,  $RH=36.3\%$ ). The nucleation was completely removed under condition B ( $T=44.3^{\circ}\text{C}$ ,  $RH=81.2\%$ ; see Fig. 8, top panel) and nearly suppressed under condition C ( $T=34.7^{\circ}\text{C}$ ,  $RH=31.6\%$ ; see Fig. 8, bottom panel).

We do not have a satisfactory explanation for the reduction of nucleation mode particles with acetone and MTBE. MTBE is an inert compound that is often used as a solvent in chemical reactions and thus, no chemical reaction with any reactive combustion product is expected.

### 3.2.5. Alcohols

A selection of alcohols with increasing hydrophobicity was chosen, methanol, 2-propanol, 1-butanol, and 1-hexanol. When alcohol was added to the dilution air, an increase of nucleation mode particles was observed. In Fig. 9, a direct comparison of all four alcohols is depicted under all three conditions. The nucleation mode particles were increased in the following order: 2-propanol > (1-butanol or methanol) > 1-hexanol. Compared to condition A ( $T=44.9^{\circ}\text{C}$ ,  $RH=36.3\%$ ) and B ( $T=44.3^{\circ}\text{C}$ ,  $RH=81.2\%$ ), the relative increase of nucleation mode particles was much less pronounced under condition C ( $T=34.7^{\circ}\text{C}$ ,  $RH=31.6\%$ ). To explain the variation of the nucleation process within the alcohols, the surface tension and water solubility of the alcohols were considered in more detail. Since the alcohols investigated have a conspicuously lower surface tension than water, a surface tension reduction of the nucleation mode particles is expected in the presence of the alcohols. The reduction of surface tension as a function of the alcohol fraction is depicted in Fig. 10 for the alcohols investigated. The surface tensions of the water-alcohol mixtures were calculated by the method of Tamura (Tamura et al., 1955). The hydrophilic hydroxyl group interacts via hydrogen bonds with the water phase while the hydrophobic rest of the alcohol is directed away from the droplet and reduced the surface tension. A reduction of surface tension increases the nucleation mode particles since the barrier to nucleate is reduced. The highest increase in nucleation occurred for 2-propanol followed by methanol, 1-butanol, and

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1-hexanol. The calculated reduction of surface tension was consistent with the observed increase of the nucleation mode particles shown in Fig. 9. No difference of methanol and 1-butanol were found because both alcohols increased nucleation mode particles to a similar level. 1-hexanol showed a distinctly lower increase of nucleation mode particles than the other investigated alcohols. In Table 5 the water solubility of the alcohols are listed. Methanol and 2-propanol containing a short hydrophobic chain are miscible with water and thus, a stronger nucleation is expected than for the more hydrophobic 1-butanol and 1-hexanol. 1-butanol showed a more pronounced growth of nucleation mode particles than 1-hexanol, which can be explained by the more than 13 times higher water solubility of 1-butanol. For the two more hydrophobic alcohols a two-phase system is expected causing a lower nucleation rate if the concentration exceeds their water solubility.

#### 4. Conclusions

The role of organic vapors in the dilution air of diesel exhaust was investigated at constant vehicle speed. Three different settings of conditions A ( $T=44.9^{\circ}\text{C}$ ,  $RH=36.3\%$ ), B ( $T=44.3^{\circ}\text{C}$ ,  $RH=81.2\%$ ), and C ( $T=34.7^{\circ}\text{C}$ ,  $RH=31.6\%$ ) were defined by the two crucial nucleation parameters, sample humidity and sample temperature. Increased humidity initiated nucleation at the higher sample temperature and increased the existing nucleation mode at the lower sample temperature. As soon as the humidity initiated the nucleation process, the nucleation particles concentration showed a linear correlation with relative humidity of the sample. The increase of nucleation mode particles at a sample temperature of  $44.9^{\circ}\text{C}$  was about 40% higher than at a sample temperature of  $34.7^{\circ}\text{C}$ .

It was observed that organic compounds played a key role in nucleation. Because there is little knowledge of the chemical composition of the organic compounds involving in the formation of nucleation particles, we studied a broad selection of organic compounds. Aliphatic hydrocarbons (hexane and cyclohexane) turned out to be with-

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out effect on the nucleation process due to their high volatility. The hydrophobic toluene could initiated and slightly increased a pre-existing nucleation mode at high concentration. However, hydrophobic compounds without any functional groups and with vapor pressure equal or higher than toluene are unlikely to substantially contribute to the nucleation mode particles of diluted diesel exhaust. Aniline was capable of reducing the nucleation mode particles. Because of its basic character, aniline is proposed to neutralize the sulfuric acid and prevent nucleation of sulfuric acid and water. Alcohols generally increased nucleation mode particles. Two parameters affected the potential of nucleation, reduction of surface tension and water solubility. Increasing water solubility and decreasing surface tension led to stronger nucleation. 2-propanol, with the highest reduction in surface tension and water miscibility, increased nucleation most. The lower potential for nucleation of the water miscible methanol can be explained by the lower reduction of the surface tension compared to 2-propanol. Nucleation mode particles were less influenced by the more hydrophobic 1-hexanol. Although 1-hexanol and 1-butanol reduce the surface tension to a comparable extent, 1-butanol increased the concentration of nucleation mode particles significantly more than 1-hexanol. A possible reason for this finding could be the 13 times higher water solubility of 1-butanol. Acetone and MTBE reduced nucleation mode particles; we presently do not have any satisfactory explanation for this behavior. In the case of MTBE, the nucleation could be suppressed almost completely. Further work has to be undertaken to understand the influence of organic compounds in reduction of nucleation mode particles in more detail.

*Acknowledgements.* This project was funded by the Swiss Federal Office for Education and Science (BBW). We thank R. Crockett from EMPA for critical review.

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displacement per cylinder	1896 cm <sup>3</sup>
number of cylinder	4
maximum power/rpm	81 kW/4150 min <sup>-1</sup>
aftertreatment system	oxidation catalyst
model year	1999

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**Table 2.** Fuel analysis of the diesel.

analysis	unit	result
sulfur	ppm	323
cetan index	–	49.1
density at 15°C	kg m <sup>-3</sup>	831
viscosity at 40°C	mm <sup>2</sup> s <sup>-1</sup>	2.41
flash point	°C	62.5
aromatics	volume-%	24.7

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**Table 3.** Average and standard deviation of the key parameters for all test series.

compound	dilution ration	relative humidity (RH)	sample temperature (T)	exhaust temperature	number of measurements
<b>condition A</b>					
hexane	8.1±0.1	37.2±0.5	45.0 <sup>a</sup>	149.4±0.1	3
cyclohexane	8.0±0.2	38.2±0.9	45.0 <sup>a</sup>	149.3±0.2	5
toluene	8.0±0.1	36.5±0.4	45.2 <sup>a</sup>	150.7±0.3	8
aniline	8.1±0.0	35.9±0.0	45.9 <sup>a</sup>	150.7±0.1	3
acetone	8.0±0.1	36.8±0.3	45.8±0.4	151.1±0.2	4
MTBE	8.1±0.1	36.4±0.2	44.7±0.8	151.1±0.2	5
methanol	8.4±0.1	35.9±0.4	45.6±1.1	153.1±0.2	8
2-propanol	8.1±0.1	36.8±0.2	45.0±0.2	153.1±0.4	5
1-butanol	8.3±0.1	36.1±0.2	44.7±0.1	151.6±0.2	5
1-hexanol	8.2±0.1	36.6±0.4	44.8±0.0	151.8±0.3	5
average	8.2±0.2	36.3±0.9	44.9±0.7	150.8±1.7	51
<b>condition B</b>					
hexane	8.3±0.1	80.7±0.2	45.2 <sup>a</sup>	150.0±0.2	3
cyclohexane	8.4±0.1	81.7±0.1	44.8±0.1	150.2±0.2	3
toluene	8.2±0.1	80.9±0.8	44.7±0.5	148.0±0.2	8
aniline	8.1±0.4	82.1±1.5	43.1±0.2	157.9±0.1	4
acetone	8.3±0.1	84.4±1.9	43.0±0.1	149.3±0.3	5
MTBE	8.3±0.1	82.3±0.6	43.1 <sup>a</sup>	149.7±0.	3
methanol	8.7±0.1	81.8±0.5	44.7±0.4	152.6±0.3	7
2-propanol	8.6±0.1	81.9±0.7	44.5±0.1	153.0±0.2	5
1-butanol	8.5±0.1	82.1±0.5	44.6±0.1	152.9±0.2	6
1-hexanol	8.3±0.9 <sup>b</sup>	85.2±3.2	45.1±0.3	153.0±0.2	5
average	8.4±0.2	81.2±3.8	44.3±0.9	151.1±2.7	49

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






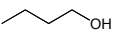
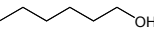
compound	dilution ratio	relative humidity ( <i>RH</i> )	sample temperature ( <i>T</i> )	exhaust temperature	number of measurements
<b>condition C</b>					
hexane	8.3±0.1	32.2±0.3	34.4±0.2	158.7±0.1	5
cyclohexane	8.4±0.1	31.5±0.3	34.2±0.1	159.0±0.1	2
toluene	8.5±0.1	31.0±0.3	34.3±0.1	158.7±0.3	6
aniline	8.3±0.0	32.6±0.2	35.1±0.6	158.7±0.2	6
acetone	8.3±0.1	31.5±0.4	34.2±0.4	159.4±0.2	6
MTBE	8.1±0.1	32.1±1.2	35.8±1.5	149.9±0.3	9
methanol	8.6±0.1	31.0±0.2	35.0±0.1	154.9±0.1	6
2-propanol	8.2±0.1	31.6±0.3	34.9±0.5	150.1±0.4	8
1-butanol	8.6±0.1	31.0±0.4	35.1±0.1	154.6±0.2	5
1-hexanol	8.5±0.1	31.1±0.3	35.1±0.2	153.8±0.7	5
average	8.4±0.1	31.6±0.6	34.7±0.5	155.3±3.9	58

<sup>a</sup> The dilution temperature was only once measured during the whole test and thus, no deviation is indicated.

<sup>b</sup> Bigger deviation was due to the lower dilution ratio of 6.7 in the first SMPS scan.

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**Table 4.** Molecular structure of the investigated organic compounds.

compound	structure
hexane	
cyclohexane	
toluene	
aniline	
acetone	
methyl tert-butyl ether (MTBE)	
methanol	
2-propanol	
1-butanol	
1-hexanol	

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**Table 5.** Water solubility of the investigated alcohols (CRC-press, 1985).

alcohol	water solubility, 20°C
methanol	completely miscible
2-propanol	completely miscible
1-butanol	77 g l <sup>-1</sup>
1-hexanol	5.8 g l <sup>-1</sup>

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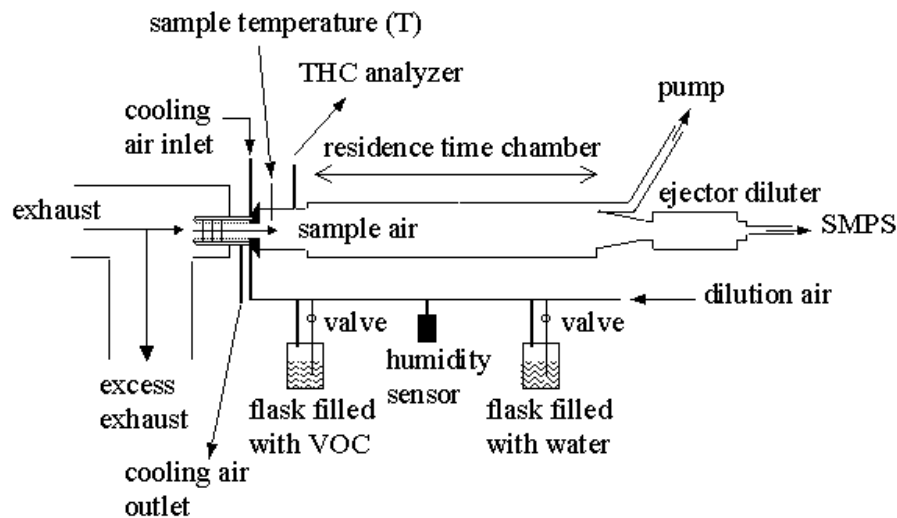
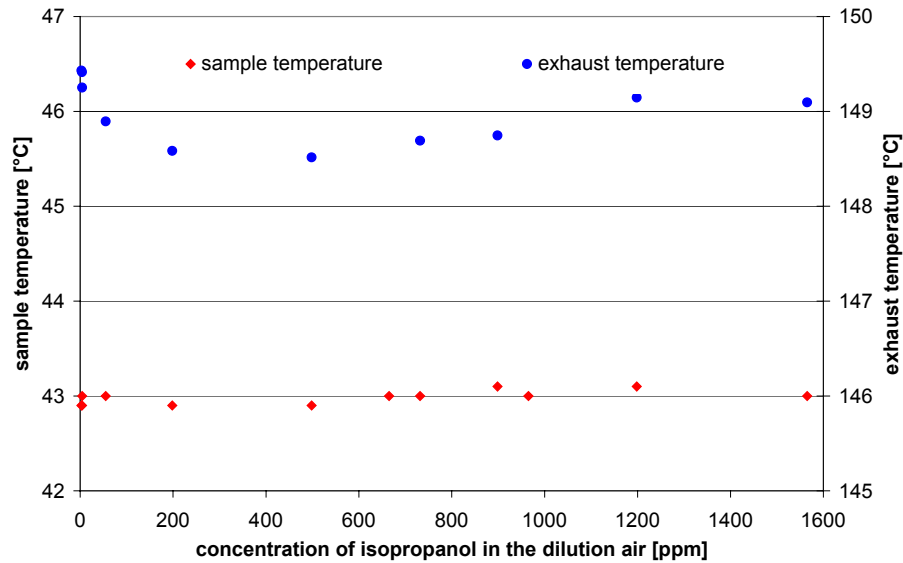


Fig. 1. Overview of the experimental set-up.

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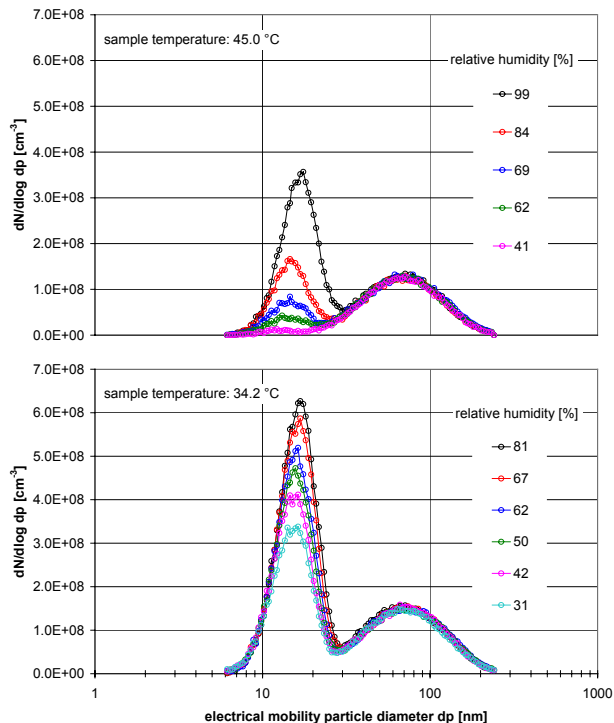


**Fig. 2.** Variation of sample and exhaust temperatures as a function of the 2-propanol concentration in the sample air.

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**Fig. 3.** Influence of humidity on the nucleation mode. A weak nucleation was detected at the lowest relative humidity of 41% and sample temperature  $45.0\text{ }^{\circ}\text{C}$ . The nucleation increased more than one order of magnitude when the relative humidity increased to 99%. For the sample temperature  $34.2\text{ }^{\circ}\text{C}$  a nucleation mode was observed even with the lowest relative humidity 31%. Therefore, the increase of nucleation was less pronounced than at sample temperature  $45.0\text{ }^{\circ}\text{C}$ .

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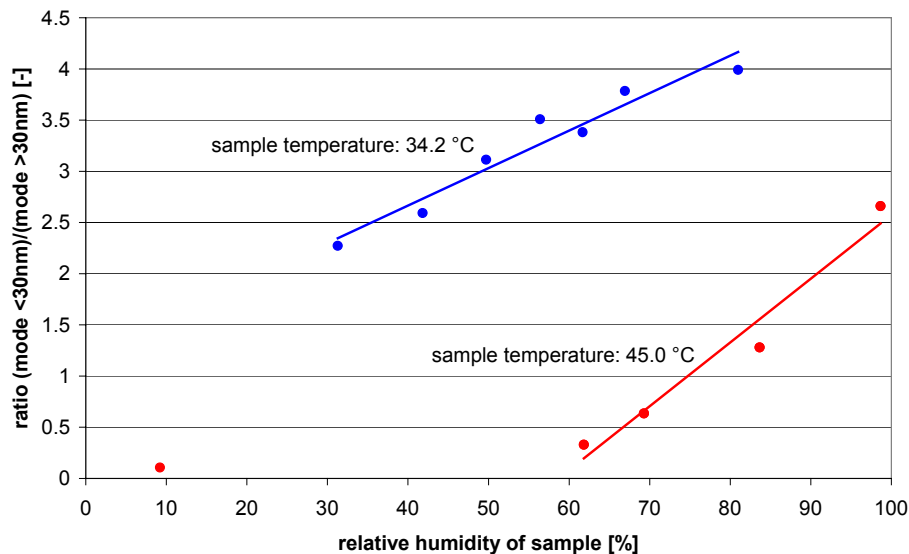
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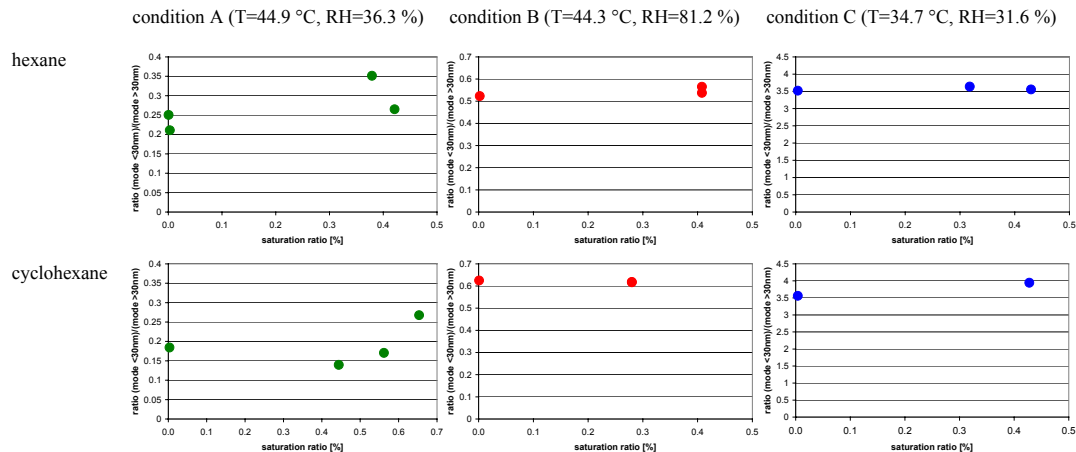


**Fig. 4.** Strength of nucleation for variable humidity. The linear regression in the linear region resulted in a correlation factor of  $R^2=0.94$  and  $R^2=0.96$  at sample temperature  $34.2^\circ\text{C}$  and  $45.0^\circ\text{C}$ , respectively.

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**Fig. 5.** Effect of the investigated organic compounds on the nucleation mode particles under condition A, B and C.

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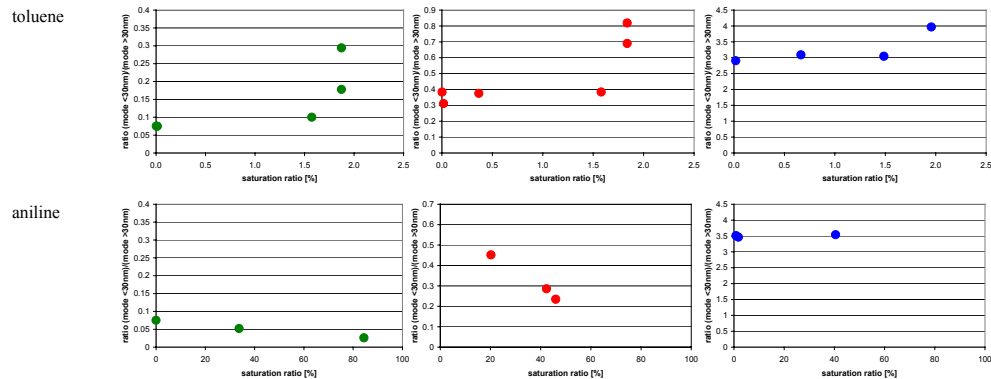


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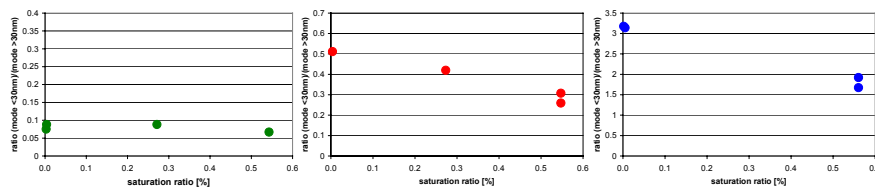
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acetone



methyl tert-butyl ether (MTBE)

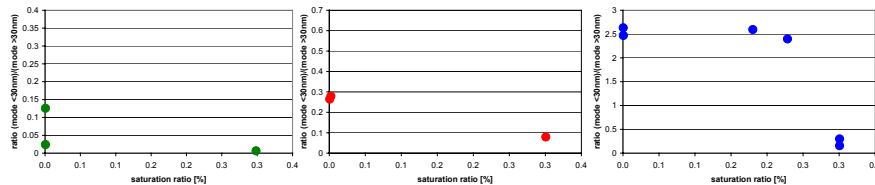


Fig. 5. Continued.

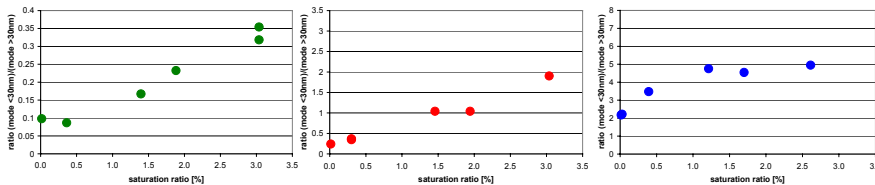
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methanol



2-propanol

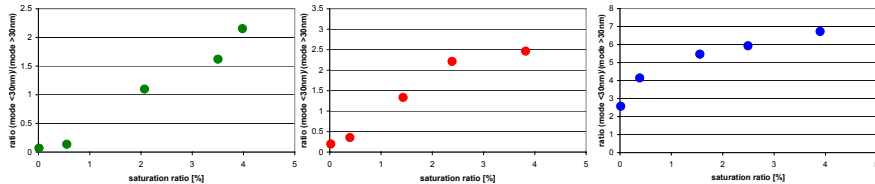


Fig. 5. Continued.

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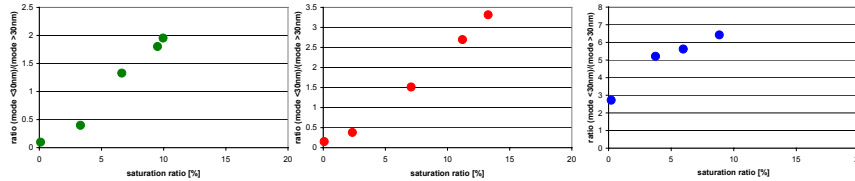
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1-butanol



1-hexanol

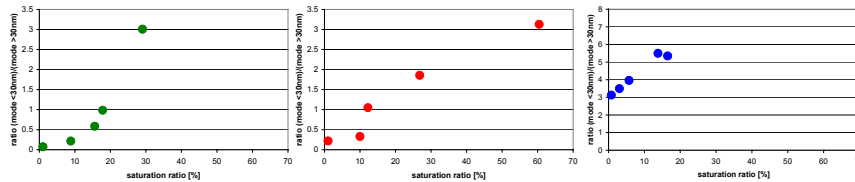
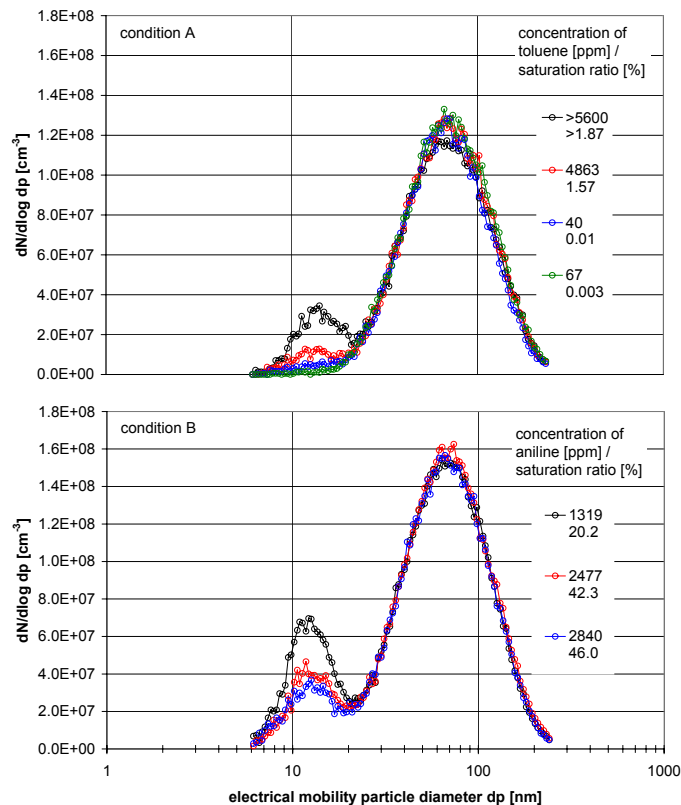


Fig. 5. Continued.

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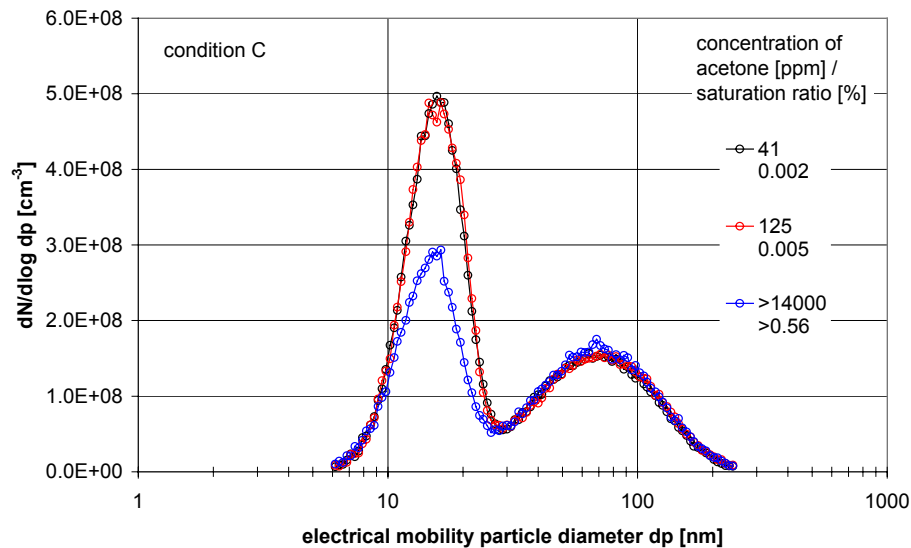


**Fig. 6.** Particle size distribution in the presence of aromatic compounds. The effects on the nucleation mode particles are presented for toluene (top panel) and aniline (bottom panel) under condition A ( $T=44.9^{\circ}\text{C}$ ,  $RH=36.3\%$ ) and B ( $T=44.3^{\circ}\text{C}$ ,  $RH=81.2\%$ ), respectively.

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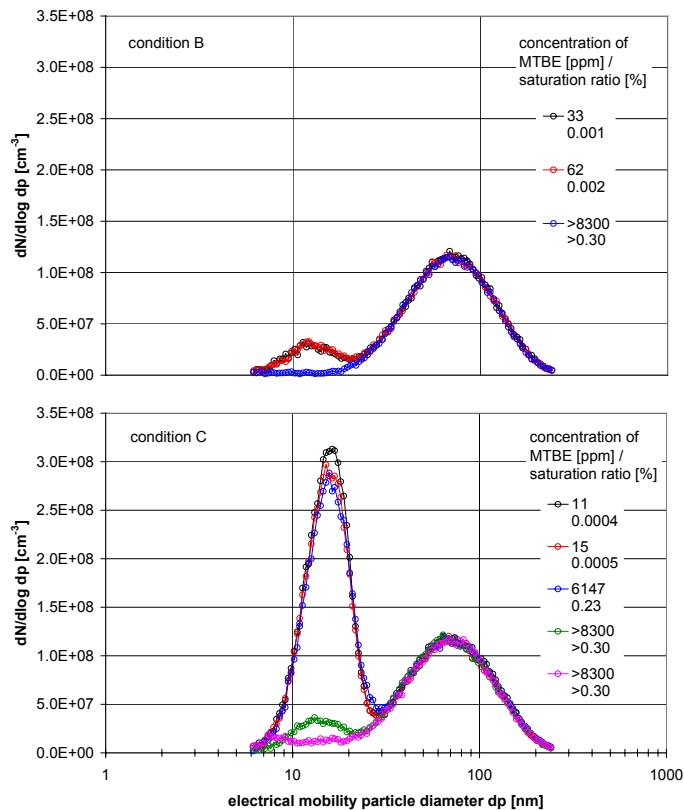


**Fig. 7.** Particle size distribution in the presence of acetone. Reduction of the nucleation mode particles occurred under condition C ( $T=34.7^{\circ}\text{C}$ ,  $RH=31.6\%$ ).

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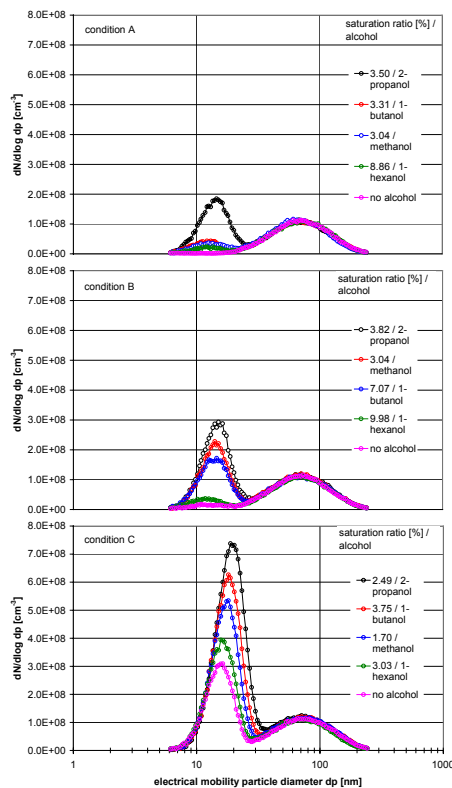


**Fig. 8.** Particle size distribution in the presence of MTBE under condition B ( $T=44.3^{\circ}\text{C}$ ,  $RH=81.2\%$ ) and C ( $T=34.7^{\circ}\text{C}$ ,  $RH=31.6\%$ ) on top panel and on bottom panel, respectively. In both cases the nucleation mode particles were reduced.

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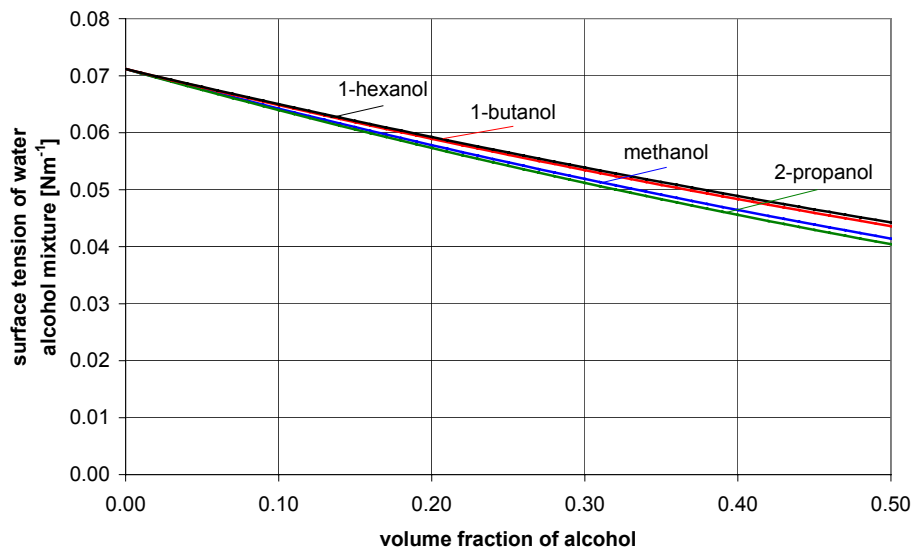


**Fig. 9.** Particle size distribution in the presence of methanol, 2-propanol, 1-butanol, and 1-hexanol under all three conditions A ( $T=44.9^\circ\text{C}$ ,  $RH=36.3\%$ ), B ( $T=44.3^\circ\text{C}$ ,  $RH=81.2\%$ ) and, C ( $T=34.7^\circ\text{C}$ ,  $RH=31.6\%$ ).

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**Fig. 10.** Surface tension of water-alcohol mixtures versus on the alcohol volume concentration.

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