



LUND UNIVERSITY

Chemical composition and mass emission factors of candle smoke particles

Pagels, Joakim; Wierzbicka, Aneta; Fors, Erik; Isaxon, Christina; Dahl, Andreas; Gudmundsson, Anders; Swietlicki, Erik; Bohgard, Mats

Published in:
Journal of Aerosol Science

DOI:
[10.1016/j.jaerosci.2008.10.005](https://doi.org/10.1016/j.jaerosci.2008.10.005)

2009

Document Version:
Peer reviewed version (aka post-print)

[Link to publication](#)

Citation for published version (APA):
Pagels, J., Wierzbicka, A., Fors, E., Isaxon, C., Dahl, A., Gudmundsson, A., Swietlicki, E., & Bohgard, M. (2009). Chemical composition and mass emission factors of candle smoke particles. *Journal of Aerosol Science*, 40(3), 193-208. <https://doi.org/10.1016/j.jaerosci.2008.10.005>

Total number of authors:
8

General rights

Unless other specific re-use rights are stated the following general rights apply:
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

Read more about Creative commons licenses: <https://creativecommons.org/licenses/>

Take down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

LUND UNIVERSITY

PO Box 117
221 00 Lund
+46 46-222 00 00

1
2 **CHEMICAL COMPOSITION AND MASS EMISSION FACTORS OF**
3 **CANDLE SMOKE PARTICLES**

4
5 JOAKIM PAGELS^{1,*}, ANETA WIERZBICKA¹, ERIK NILSSON^{1,2}, CHRISTINA ISAXON¹,
6 ANDREAS DAHL¹, ANDERS GUDMUNDSSON¹, ERIK SWIETLICKI² AND MATS BOHGARD¹

7
8 1. Ergonomics and Aerosol Technology (EAT), Lund University, P.O. BOX 118, SE-221 00 Lund, Sweden.

9 2. Nuclear Physics, Lund University, P.O. BOX 118, SE-221 00 Lund, Sweden.

10
11 *Corresponding author. Tel.: +46-46-222-16-88; fax: +46-46-222-44-31

12 *E-mail address:* joakim.pagels@design.lth.se (J. Pagels)

13
14 **KEYWORDS:** AEROSOL, CANDLES, INDOOR AIR, SOOT, MASS CLOSURE, ULTRAFINE
15 **PARTICLES**

16
17 **Abstract**

18 The aim of this study is to investigate the physical and chemical properties of particle emissions from
19 candle burning in indoor air. Two representative types of tapered candles were studied during steady burn,
20 sooting burn and smouldering (upon extinction) under controlled conditions in a walk-in chamber. Steady
21 burn emits relatively high number emissions of ultrafine particles dominated by either phosphates or alkali
22 nitrates. The likely source of these particles is flame retardant additives to the wick. Sooting burn in
23 addition emits larger particles mainly consisting of agglomerated elemental carbon. This burning mode is
24 associated with the highest mass emission factors. Particles emitted during smouldering upon extinction
25 are dominated by organic matter. A mass closure was illustrated for the total mass concentration, the
26 summed mass concentration from chemical analysis and the size-integrated mass concentration assessed

1 from number distribution measurements using empirically determined effective densities for the three
2 particle types.

3 **1. Introduction**

4 A significant fraction of the exposure to fine and ultrafine particles occurs indoors in the home and other
5 indoor environments, as people spend more than 85% of the time in indoor environments (Klepeis et al.
6 2001). The indoor exposure includes particles infiltrating from outdoor air and indoor particle sources.
7 Many epidemiological studies linking particle exposure to adverse health effects have been made in
8 outdoor air, partly due to the relative ease of using data from central monitoring stations outdoors in large
9 populations within a city. While the characteristics of ambient particles have been studied extensively, the
10 contributions to the exposure from individual indoor particle sources are poorly known. There may also be
11 significant differences between particles of indoor and outdoor origin in terms of particle chemical
12 composition, size distribution and morphology, properties likely to be important in controlling adverse
13 health effects.

14
15 In several field studies in homes, candles have been identified as sources of ultrafine particles (Matson
16 2005, Hussein et al. 2006, Wierzbicka et al. 2008), larger accumulation mode particles (Ogulei et al. 2006,
17 Long et al. 2000) and a major contributor to indoor Elemental Carbon (EC) and PM_{2.5} concentrations
18 (Sørensen et al. 2005, Larosa et al. 2002). Candle burning has also been associated with black spot
19 formation on walls and staining of ancient paintings, sculptures and tapestries in churches (Hyunh et al.
20 1991; Edwards et al. 2005; Perez et al. 1999).

21
22 Candles have been used since ancient times as a source of light and are today commonly used for aesthetic
23 and religious purposes in various indoor environments. Already in 1860 Michel Faraday described
24 mechanisms of the combustion taking place in a candle flame in his lecture notes on “the chemistry of
25 candles”. The candle flame can be approximated as a diffusion flame, with the wax serving as fuel and the
26 wick serving as transport mode of the fuel by capillary forces. Air is the oxidant, transported by

1 convection vertically along the flame. In fuel rich regions of the flame, large quantities of soot particles
2 form. The yellow incandescent light making up the majority of the flame is the result of soot oxidation in
3 the flame. During normal steady burn, in principle all soot formed in the flame can be oxidised, resulting
4 in very low EC emissions. However, horizontal air movements in the vicinity of the flame, for example
5 due to an open window, may result in a flickering flame and some soot being able to escape without being
6 oxidised. This we refer to as sooting burn mode. Another mode of burning is smouldering upon extinction
7 of the candle producing visible white smoke.

8
9 There are several different types of additives used in candles to improve the burning performance and
10 aesthetic appearance (Knight et al. 2001). For example alkanolic acids such as stearic acid are used to
11 improve hardening characteristics of the wax and increase the melting point. Added colouring pigments
12 may contain heavy metals. Inorganics such as ammonium phosphates and borax (a salt mixture containing
13 borates) are added to the wick to act as a flame retardants to ensure that the wick is consumed at a
14 sufficient rate and to prevent glowing of the wick upon extinction. In certain types of candles, metals such
15 as zinc, tin and lead are added to the wick to improve mechanical stability. More recently fragrance oils
16 have been added to certain types of candles.

17
18 A potential health problem related to candle burning is the occurrence and release of metal additives from
19 the wick and colour pigments. Several studies have focused on lead and other heavy metal emissions from
20 metal-cored candles (Van Alphen 1999, Nriagu and Kim 2000, Wasson et al. 2002, Lin et al. 2003).
21 Wasson et al. (2002) found relatively high lead emission rates of 0.1-1.7 mg h⁻¹ in 8 out of 100 purchased
22 candles. Burning of such high emitting candles can easily lead to exceedance of ambient air lead
23 concentration limits, for example 1.5 µg m⁻³ set by the US EPA. They also showed that 8-23% of the lead
24 in the wick was released as fine particles, while the rest was retained in the ash in the wax pool. For
25 example in the USA, candle wicks containing lead are uncommon after agreements between national
26 manufacturers to discontinue the use of lead as a core material (Knight et al. 2001). Replacements for lead

1 in metal-cored candle wicks include zinc and tin. Zinc emission factors up to 0.12 mg h^{-1} were identified
2 by Nriagu and Kim (2000).

3
4 Lau et al. (1997) investigated emissions of Polycyclic Aromatic Hydrocarbon (PAH) emissions and gas-
5 phase Volatile Organic Carbon (VOC). They found that candles have low PAH and VOC emission levels
6 compared to other indoor combustion sources. This is likely caused by the high combustion temperature
7 and relatively complete combustion occurring in a steady burning candle.

8
9 Li and Hopke (1993) studied particle emissions from a steady burning single paraffin wax candle and
10 found that the initial size distribution was dominated by ultrafine particles of around 30 nm in diameter.
11 Their study focused on the hygroscopic growth of particles measured at a relative humidity similar to that
12 occurring in the human respiratory tract. They found diametric hygroscopic growth factors of around 2.2
13 at RH=99.0-99.5%, which is significantly higher than for most known organic compounds and elemental
14 carbon. They speculated that the presence of organic acids were responsible for the high particle growth.

15
16 Afshari et al. (2005) studied number concentrations emitted from two “pure wax” candles and two scented
17 candles separately in a 32 m^3 chamber (air exchange rate 1.7 h^{-1}) and found maximum number
18 concentrations of $240000 \text{ particles cm}^{-3}$ and $69000 \text{ particles cm}^{-3}$ respectively, for the two candle types
19 measured with a condensation particle counter (particles $> 20 \text{ nm}$).

20
21 Fine, Cass and Simoneit (1999) focused on detailed analysis of organic compounds present in the particle
22 phase of emissions from a paraffin and a beewax candle. They found that sooting burn conditions are
23 associated with relatively high elemental carbon emissions. During sooting burn an additional larger sized
24 particle mode above 100 nm appears in mobility size distribution measurements in addition to the ultrafine
25 mode. Organic carbon emissions were mainly associated with smouldering burning upon candle
26 extinction; similarly a larger mode above 100 nm occurred during smouldering. Gravimetrically

1 determined emission factors associated with extinguishing one candle were 0.6-1.8 mg, while sooting burn
2 led to an emission factor as high as 26 mg h⁻¹. Through detailed GC/MS analysis they showed that the
3 particle phase organics in the candle smoke consist of a combination of unaltered fuel which has
4 undergone evaporation and condensation and partly oxidized fuel. There were relatively large differences
5 in organic composition between the paraffin and the beewax candle smoke, due to differences in the fuel
6 composition. Based on their data the chemical composition of the small ultrafine particles dominating the
7 “efficient burning” mode could not be determined.

8
9 Fan and Zhang (2001) used a nephelometer to assess mass emission factors of 3.4 mg h⁻¹ for unscented 7.6
10 cm diameter paraffin candles. Zai et al. (2006) used another nephelometric device to determine emission
11 factors of a single tapered candle made of paraffin wax during three different burn conditions. During
12 steady burn, emission factors were low (0.33 mg h⁻¹), while higher emissions of 7.6 mg h⁻¹ were found
13 during sooting burn. However, the response of nephelometers depends strongly on the optical particle
14 properties which in turn are a strong function of particle size, morphology and chemical composition.
15 Particularly the response to ultrafine particles ($d_p < 100$ nm) is very low compared to larger sizes.

16
17 Although efforts have been made to characterize particle emissions from candles in several studies, there
18 are still significant knowledge gaps, especially regarding the composition and concentration of particles
19 emitted during the different modes of burning. For example, the composition of the ultrafine particles
20 which appear in very high number concentrations during steady burning is not known. To our knowledge
21 no study has performed measurements of inorganics (except for heavy metals such as lead and zinc) which
22 are present in the candle as additives and may become airborne through volatilization and condensation or
23 through heterogeneous reactions in the gas-phase. Furthermore, there are no reported studies of the
24 morphology of particles from different burning conditions.

25

1 The aim of this paper is to investigate the chemical composition, morphology and mass emission factors
2 during three different modes of burning. Another aim is to establish effective density factors to allow
3 assessments of the particle mass size distribution using a Scanning Mobility Particle Sizer and to compare
4 mass concentrations using different instrumental approaches.

5 **2. Materials and Methods**

7 **2.1. Experiment chamber**

8 Candle smoke was generated in a 21.6 m³ stainless steel chamber (Figure 1). The RH in the chamber was
9 controlled to 30 ± 5% and the temperature was 23-28 °C. The temperature typically increased during an
10 experiment due to the energy released as heat from the candles. The supply air flow rate was determined
11 from pressure drop measurements at the entrance to the chamber. The flow rate was 10.8 m³ h⁻¹, which
12 corresponds to an air exchange rate of 0.5 h⁻¹. The supply air passed an activated carbon filter to remove
13 VOCs and oxidants and an ULPA (Ultra Low Penetration Air filter) particle filter. Air to the chamber was
14 supplied from the roof while the exhaust was positioned in the opposite corner from the supply at a height
15 of 0.5 m from the floor. The exhaust fan was adjusted until a positive pressure difference between the
16 chamber and the surrounding air of 5-10 Pa was established. Inside the chamber a revolving fan (model
17 A540, Appliance Inc.) was operated to ensure complete mixing. The fan was operated at the lowest
18 internal setting and 110 V on an external voltage supply. The resulting air velocity in the vicinity of the
19 candles was varying in a cyclical manner with a period of 25 seconds. The peak air velocity over the cycle
20 measured with an air velocity meter (model 8330, TSI Inc.) was 0.4 m s⁻¹. In between these peak velocities
21 the flow rate dropped to below 0.01 m s⁻¹. We believe these cyclic air velocities mimic typical indoor
22 convective air motion reasonably well.

23
24 The degree of mixing in the chamber was found to be complete as verified using simultaneous trace gas
25 (SF₆) measurements (model 1312 Photoacoustic Multi-gas Monitor and model 1303 Multipoint Sampler
26 and Doser, Innova AirTech Instruments) in three positions of the chamber. The chamber is entered

1 through an antechamber. The ventilation system is set up in such a way that the air leaves the main
2 chamber through the exhaust, then enters the antechamber and finally is vented away. This ensures that
3 the pollutant concentration is similar in the chamber and the antechamber, which in turn allows for an
4 operator to enter the chamber with minimum disturbances of the pollutant concentration in the main
5 chamber.

6

7 **2.2. Candle emission experiments**

8 Two different kinds of tapered candles were studied. Candles of type I were white and according to the
9 manufacturer a wax based on pure stearin is used. Candle I is in a slightly higher price range and is
10 marketed as a low soot emitting candle. According to the manufacturer type II candles are made up of a
11 wax consisting of a combination of stearin and paraffin. These candles are dark blue. Candle II is a typical
12 budget candle in a lower price range. Both candles are manufactured by market leading companies in
13 Sweden.

14

15 In each experiment, four candles of either type I or type II were put in candle holders on a table and
16 burned in the chamber. Three types of experiments were conducted: 1) “Steady burn” experiments, where
17 each candle was shielded from the convective air flows from the mixing fan using 350 mm diameter, 600
18 mm high metallic tubes made from conventional ventilation ducts. Two candles were put inside each tube
19 at a distance of more than 100 mm from each other. The flame was at a height of 100 mm or more, below
20 the top of the metal tube. A 10 mm high opening was used at the bottom of each shielding tube. This
21 reduced the degree of flickering of the flame. 2) “Sooting burn” experiments without the shielding tubes to
22 study the influence of convective air currents on soot formation. The candle flames were flickering in
23 these sets of experiments and 3) “Smouldering” experiments to study the white smoke emitted upon
24 extinction of the candles. “Steady burn” and “sooting burn” experiments were performed for both types of
25 candles, while “smouldering” experiments were only performed for candle II. All experiments were
26 repeated two to three times.

1
2 The experimental procedure involved first ventilating the chamber to a particle concentration below 1000
3 particles cm^{-3} (corresponding to a mass concentration of less than $0.1 \mu\text{g m}^{-3}$). An operator then entered
4 the chamber after waiting 20 s in the antechamber. In the chamber, the four candles were lighted using a
5 propane lighter (Multi-purpose lighter, BIC Inc.). Control experiments showed that this lighter does not
6 produce any detectable amount of particles larger than 10 nm. Particle size and mass concentration
7 measurements were started when the chamber was empty and then run continuously throughout each
8 emission experiment. Typically, filter measurements were started 15 min after the candles were ignited, to
9 allow build-up of particle concentrations in the chamber. Filter collection lasted 10-20 min in sooting burn
10 experiments and 60-80 min in steady burn experiments (to compensate for the difference in emission
11 factors). In smoulder experiments the candles were ignited and burning with shielding tubes for 10
12 minutes. Then the candles were extinguished using an inverted cup designed for this purpose. Each candle
13 was covered for 3 seconds before the inverted cup was removed. Filter collection started 5 minutes after
14 candles were extinguished and lasted for 45 minutes.

15

16 **2.3. Box model for determination of emission factors**

17 A simple box model was used to estimate mass emission factors (Koutrakis et al. 1991) from the measured
18 particle concentrations in the chamber. In a well-mixed box the following mass conservation relationship
19 applies:

20

$$21 \quad \frac{dC(t)}{dt} = aC_{inc.} + \frac{E_{r,m}}{V} - (a + k)C(t) \quad (1)$$

22

23 Where $C(t)$ is the mass concentration in the chamber, $C_{inc.}$ is the concentration in the incoming air, a is the
24 air exchange rate (h^{-1}), k is the sum of other loss mechanisms (h^{-1}), for example wall losses, $E_{r,m}$ is the
25 mass emission factor (mg h^{-1}) and V is the volume of the chamber. It should be noted that k typically is

1 particle size dependent. In our experiments the concentration in the incoming air was negligible (below
2 $0.01 \mu\text{g m}^{-3}$) so C_{inc} could be set to zero. Assuming that the initial concentration is zero and that $E_{r,m}$ is
3 constant over time, Eq. 1 has the following solution:

4

$$5 \quad C(t) = \frac{E_{r,m}}{V(a+k)} \cdot (1 - e^{-(a+k)t}) \quad (2)$$

6

7 The total loss rate $(a+k)$ as a function of particle size was determined from decay experiments at low
8 concentrations ($< 5\,000 \text{ particles cm}^{-3}$), where coagulation can be neglected (coagulation is a mass
9 conserving loss mechanism, which should not be included in k when calculating mass emission factors).
10 All factors on the right-hand side except the emission factor are then known. These experiments were
11 made in connection to the real sooting burn emission tests. After filter sampling was finished, the chamber
12 was express ventilated for about 15 min (AER 15 h^{-1}), in this time some small particles were lost through
13 coagulation but the size distribution was still qualitatively similar to the high concentration tests.

14

15 For on-line measurements $E_{r,m}$ was fitted to experimental data using Eq. 2. For chemically resolved off-
16 line filter experiments, first the (average) measured mass concentration over the measurement interval was
17 calculated. The predicted average concentration over the measurement period was then calculated using
18 the model and $E_{r,m}$ was finally varied until the measured and modelled average concentrations agreed. This
19 approach gives the average emission factor over the measurement interval. The value of $a+k$ used in Eq. 2
20 was determined using the average mass geometric mean diameter determined from SMPS measurements
21 for a given experiment. At 100 nm the value of $a+k$ was 0.65 h^{-1} indicating that the major loss rate was
22 due to the ventilation system. At 30 nm $a+k$ increased to 1.2 h^{-1} . Emission factors were derived over the
23 time-intervals of the filter measurements to allow comparison between the different techniques. This was
24 typically done over the first two hours of an experiment. Note that equilibrium concentrations in the
25 chamber are not reached at this time.

1

2 **2.4. Particle characterization**

3 The mobility particle size distribution was measured using an electrical mobility spectrometer (SMPS
4 3934, TSI Inc.). The instrument consisted of a bipolar charger (^{63}Ni approximate Nt-product 2×10^8
5 cm^3/s), a long column Differential Mobility Analyzer (LONG DMA, TSI Inc.) and a Condensation
6 Particle Counter (CPC model 3010, TSI Inc.). It was used in a closed loop set-up with a sheath flow rate
7 of 2.4 lpm and an aerosol flow rate of 0.4 lpm. These flows enabled measurements of a particle size range
8 between 16 and 1000 nm. The size range up to 1000 nm was important in determining mass size
9 distributions of soot and smoulder particles. The scan times were 180 s up and 30 s down. Critical orifices
10 were used in the closed loop downstream the DMA and downstream the CPC to assure stable flows. A
11 make-up flow of 0.6 lpm which passed a High Efficiency Particulate Air (HEPA) filter was used to add up
12 to the nominal CPC flow rate of 1.0 lpm. The make-up flow rate, the DMA inlet flow rate and the sheath
13 flow rates were measured using a bubble flow meter (medium cell, Gillian Inc.) before and after each
14 experiment.

15

16 In a few experiments a Thermodesorber (TD) was added upstream the SMPS system. We refer to this
17 combination as Volatility-SMPS. The TD enabled us to evaporate volatile particle constituents in the
18 temperature range 30-450 °C. The TD is similar to that described by Burtscher et al. (2001). In this set-up
19 the SMPS consisted of a long DMA and an ultrafine CPC (model 3025, TSI Inc.). The DMA was operated
20 with a sheath flow rate of 20 lpm and an aerosol flow rate of 1.5 lpm. The measurement range of this
21 system was 7-200 nm. A computer controlled switching valve was used to allow a measurement sequence
22 involving one Volatility-SMPS scan passing the TD followed by two scans with the sample bypassing the
23 TD. This sequence was repeated for six TD temperatures between 30 °C and 425 °C. The size-integrated
24 particle effective volume concentration was calculated for TD and by-pass measurements, respectively.
25 Finally the remaining non-volatile volume fraction as a function of temperature was determined from the

1 ratio of the calculated effective volume concentrations. In Volatility-SMPS measurements, emissions from
2 burning of a single candle were studied; all other parameters were similar to those described above.

3
4 A correction for diffusion losses in the DMA (Martinsson et al. 2001), connectors and thermodesorber was
5 applied to all measured data. Also an empirical size independent correction for losses due to
6 thermophoresis at the outlet of the TD was applied (4% losses per 100 °C in temperature difference
7 between the set temperature and the ambient temperature). These correction factors turned out to be very
8 important, especially for particle sizes below about 20 nm during the Volatility-SMPS measurements.

9
10 A Tapered Element Oscillating Microbalance (TEOM; model 1400a, R&P Inc.) was used to determine the
11 integrated particle mass concentration on-line. The instrument was operated at
12 40 °C to decrease losses of volatile organic carbon and yet be able to operate at a low relative humidity to
13 decrease influences from water adsorption to the filter material. The instrument was equipped with a PM_{2.5}
14 inlet.

15
16 Samples for elemental and organic carbon (OC/EC) and major ions were collected using a set-up which
17 involved first passing the sample through a PM₁ cyclone and then collection onto three different filters
18 (Wierzbicka et al. 2005). Two parallel sampling lines were used. One line consisted of a quartz fibre filter
19 (Tissuequartz, SKC Inc.). In the second line a Teflon filter (Zeflour, SKC Inc.) followed by a quartz
20 backup filter (Figure 1) was used. The nominal flow rate in both lines was 5.0 lpm. These flows were
21 controlled by needle valves operated as critical orifices and were measured before and after each
22 experiment using the bubble flow meter.

23
24 Prior to the experiments, the quartz fibre filters were pre-heated for four hours at a temperature of 900 °C
25 to remove organic impurities. The filters were mounted in 37 mm cassettes (3-section clear polystyrene,
26 SKC Inc.). Stainless steel support pads were used. The filter cassettes were stored before and after the

1 experiments at a temperature of 5 °C. A 0.495 cm² filter punch was obtained from each quartz filter and
2 used for the OC/EC analysis. The OC concentration detected on the back-up quartz filter was subtracted
3 from the OC concentration on the front quartz filter to correct for the positive artefact caused by
4 adsorption of gas-phase organics onto quartz filters. A thermal-optical method, using a carbon analyzer
5 developed by the Desert Research Institute was used for OC and EC analysis (Model 2001, DRI; Chow et
6 al. 1993). The Teflon filters were analysed for major water-soluble ions (F⁻, Cl⁻, SO₄²⁻, NO₃⁻, PO₄³⁻, Na⁺,
7 K⁺, NH₄⁺, Ca²⁺, Mg²⁺ and Li⁺) using ion-chromatography.

8
9 A stacked filter unit sampler (Heidam et al. 1981) was used to collect particles for Particle Induced X-Ray
10 Emission (PIXE) analysis. Polycarbonate filters (diameter 47 mm) with pore sizes of 8 µm and 0.4 µm
11 were used in the first and second filter stages respectively. In the first stage, particles larger than about 2.5
12 µm are collected, while smaller particles are collected in the second stage.

13
14 A small deposit area low-pressure cascade impactor (SDI Impactor) was used to collect size-fractionated
15 samples for PIXE analysis. The impactor divides the incoming particles into
16 12 stages dependent on the aerodynamic equivalent diameter and covers the particle size range
17 45 nm to 10 µm. The impactor flow rate is 11 lpm. Each experiment lasted 60 minutes.

18
19 Samples for Transmission Electron Microscopy (TEM) were collected onto electron microscopy-grids
20 using an electrostatic precipitator (NAS model 3089, TSI Inc.). The sample first passed an external
21 unipolar charger to increase the average particle charge and thereby increase the collection efficiency. The
22 morphology of the candle particles was studied using a 300 kV transmission electron microscope (model
23 3000F, JEOL Inc.).

24
25 **2.5. Method to determine mass size distributions using combined SMPS and TEOM data**

1 A model was used to make a mass closure between TEOM, filter measurements and the SMPS
2 measurements. To determine the SMPS mass size distribution, the SMPS number size distribution in each
3 experiment was first weighted by “effective volume”. The effective volume, V_{eff} , of a particle is given by

$$V_{eff}=d_p^3 \cdot \pi/6 \quad (3)$$

4
5
6
7 where d_p is the mobility diameter. The effective volume equals the true volume for spherical particles with
8 no voids but exceeds the true volume for non-spherical particles. Three lognormal modes were fitted to the
9 effective volume distribution. A least-squares, non-linear method was used to fit the three different
10 parameters for each mode ($V_{eff,n}$, GMD_n , and GSD_n) to the size distribution data. To determine the mass
11 size distribution, these lognormal modes were assigned different empirically determined effective
12 densities, ρ_{eff} , (the particle mass, m , is given by $m=\rho_{eff} \cdot V_{eff}$). For soot particles a size dependent effective
13 density was used (Park et al. 2003).

14
15 In calculating the particle mass from SMPS number distributions, instrumental errors both from number
16 concentration measurements and particle sizing contributes to the overall uncertainty. Particularly, the
17 sizing error can cause a substantial uncertainty in particle mass and effective density determinations due to
18 the cubic dependence of particle diameter. To minimize such errors the instrument combination of SMPS
19 and TEOM was calibrated using liquid spherical Di-ethyl-hexyl sebacate (DEHS) aerosol. Calibration
20 aerosol was generated using an evaporation-condensation method (model SLG-270, TOPAS GmbH)
21 operated without seed-aerosol. An aerosol with a mass median diameter of 150 nm and a Geometrical
22 Standard Deviation (GSD) of 1.4 was generated. The size distribution of the aerosol was completely
23 within the measurement range of the SMPS. The experimentally found density of DEHS was calculated
24 from the TEOM mass concentration divided by the SMPS volume. It was compared with the known
25 density ($0.91 \times 10^3 \text{ kg m}^{-3}$). A correction factor was derived to correct for a slight mismatch between the

1 two instruments. It was typically on the order of 1.2 and was applied to all mass and effective density data

2 involving the SMPS.

3

4

5

3. Results and Discussion

3.1 Particle number concentration and size distribution

Average number weighted size distributions from steady burn and sooting burn experiments are given in Figure 2. It can be seen that high number concentrations of ultrafine particles (< 100 nm) were generated. The total measured particle number concentration (16-1000 nm) was 1.14×10^6 particles cm^{-3} for candle I and 0.51×10^6 for candle II during steady burning. During sooting burn it was 0.89×10^6 and 0.27×10^6 particles cm^{-3} for candle I and II, respectively. In steady burn experiments, freshly generated ultrafine particles occurred in the peak with GMD of 20-30 nm, while the larger sizes up to about 150 nm are caused by growth, mainly from coagulation as the aerosol ages in the chamber.

In sooting burn experiments without the flow shield, the concentration in the “soot mode” with a GMD of 270 ± 30 nm (GSD 1.73 ± 0.08) increased by about two orders of magnitude in comparison to steady burn. Fine et al. (1999) and Zai et al. (2006) also found a larger sized mode during sooting burn. The number concentration in the ultrafine mode was lower in sooting burn compared to steady burn, especially for candle II. This was likely due to coagulation of formed ultrafine particles with soot mode particles.

In the smoulder experiments, the candles were burning steady for 10 minutes with flow shields. After that they were extinguished. Only candle II was studied. The influence of extinguishing the candle on the number size distribution is given in Figure 3. The particles in the ultrafine mode were mainly emitted during the period of steady burning. Upon extinction a strong increase in the concentration of particles in the larger mode with GMD 335 ± 30 nm (GSD 1.56 ± 0.04) was found.

We believe that computing number emission factors for these data would not be fully relevant. Number emission factors derived with four candles burning in these experiments would be strongly affected by coagulation. For example, the apparent number emission factor for each of the four candles would be

1 lower than in an experiment with a single candle. In a real setting the internal volume would be larger,
2 decreasing the magnitude of coagulation leading to a higher apparent number emission factor. Coagulation
3 also causes particle sizes in the chamber to increase, especially for the ultrafine mode compared to burning
4 of a single candle. Coagulation decreases the particle concentration both in the plume just above the
5 candle on short time-scales and upon dilution in the room air on longer time-scales.

6
7 Ultrafine particles emitted in typical indoor environments may be effectively scavenged by coagulation
8 with larger particles in indoor air. However, the number emission factors from candles are so high that
9 elevated concentrations of ultrafine particles will be present in most indoor environments. However, very
10 high concentrations of accumulation mode particles from sooting burn or other strong indoor sources, may
11 act as a very strong scavenger and then most ultrafine particles would quickly coagulate with pre-existing
12 particles.

13 14 **3.2. Particle morphology**

15 Particles emitted during sooting burn were collected onto EM grids and the morphology was studied using
16 TEM. In Figure 4, representative samples are shown at different degrees of magnification. The particles
17 were highly agglomerated, with clearly discernable primary particles. Similar morphology and sizes were
18 identified in samples from both candles I and II. The average primary particle diameter was 25-30 nm,
19 similar to soot in diesel exhaust (Park et al. 2004). One difference compared to diesel soot is that the
20 mobility diameter of candle soot is on the order of 270 nm while that for diesel soot is on the order of 60-
21 80 nm (Sakurai et al. 2003). Thus, candle soot aggregates consist of a higher average number of primary
22 particles in each aggregate compared to diesel soot. Most particles found in the TEM analysis were
23 aggregate particles similar to those in Figure 4 with maximum lengths in the range 200-500 nm and
24 maximum widths at 90° angle to the maximum length of around 100-350 nm. The mobility diameter is
25 reasonably close to the average of the maximum length and the width (Park et al. 2004). Therefore the
26 qualitative results of the TEM analysis are in reasonable agreement with the GMD of the soot mode

1 particles (270 nm), determined with the SMPS. Smouldering particles were, as expected, liquid and
2 volatile and therefore difficult to analyze using TEM.

3
4 We found lower numbers of particles with sizes corresponding to the ultrafine mode in the TEM analysis
5 than expected from the SMPS measurements. A small number of crystalline graphite particles with
6 diameters 5-30 nm were found. We hypothesize that the majority of ultrafine particles were evaporated
7 upon absorption of energy from the electron beam in the microscope. This would by necessity imply that
8 the ultrafine particles have low soot content (soot is non-volatile in TEM). Another explanation could
9 perhaps be that the collection and transport efficiency of the used sampling system is low for particles in
10 the size range 20-30 nm. For example the 15-25 nm particles in the nucleation mode may have been lost in
11 the unipolar charger or not efficiently collected onto the TEM-grids in the ESP. However, future studies
12 should focus on identifying the ultrafine particles using TEM, for example using low beam intensities.

13

14 **3.3. Chemical composition and mass emission factors of candle emissions**

15 In Figure 5, mass concentrations of elemental carbon, organic matter and inorganic compounds are given
16 for the five different cases studied. The class of inorganic compounds given in Figure 5 is the sum of all
17 compounds detected with IC and PIXE. Inorganic matter can dominate the composition of candle smoke
18 emissions when emissions are dominated by the ultrafine mode. This is the case for both candles during
19 steady burning.

20

21 During sooting burn, the concentration of elemental carbon increased by more than an order of magnitude.
22 The paraffin/stearin candle (candle II) had significantly higher EC emissions than the pure stearin candle
23 (candle I). The experiments during sooting burn illustrate that elemental carbon concentrations emitted
24 from candles can be very high. In these experiments simulating a small room with relative low air
25 exchange rate, mass concentrations were up to 2000 $\mu\text{g m}^{-3}$ when four candles (candle II) were burned.

26

1 In smouldering experiments the particle composition was dominated by organic matter. The organic
2 particle emissions associated with extinguishing the candles one time, resulted in average concentrations
3 of about $100 \mu\text{g}/\text{m}^3$ over the hour following the extinction. This is much lower compared to EC emissions
4 during sooting burn. To obtain the organic matter concentration, the organic carbon concentration was
5 multiplied by 1.2. Fine et al. (1999) suggested using the factor of 1.2 due to the low fraction of oxygen in
6 wax and slightly oxidized wax molecules making up the organics released during smouldering. The
7 concentrations reported in Figure 5 are high compared to most real indoor environments, since larger
8 rooms are often used. Also pollutants will disperse through open doors between different rooms.
9 Deposition onto indoor surfaces are likely larger in field experiments compared to the chamber.

10
11 Mass emission factors corresponding to the data described above were fitted using the box model. An
12 example for TEOM data during an experiment with steady burn of candle II is illustrated in Figure 6. Two
13 different models to correct for wall losses are compared, a model where the average GMD of the whole
14 experiment was used to calculate the losses and a method where the evolving GMD from each SMPS scan
15 was used. Both methods agree well with experimental data and it was concluded that the emission factors
16 could be treated as constant over time in each experiment. The two methods agree to about 1% in fitted
17 emission factor. As the experiment showed in Figure 6 represents the largest variation over time in GMD,
18 it was concluded that the model with average GMD in each experiment was sufficient for the remaining
19 data-set. Fitted mass emission factors are given in Table 1 (steady and sooting burn) and Table 2
20 (smouldering). Total mass concentrations were determined independently using the TEOM rather than by
21 just summing the concentrations from the different filter analysis. The total mass emission factors
22 determined in this study ($0.9\text{-}25.3 \text{ mg h}^{-1}$) are significantly higher than those given by Zai et al. (2006).
23 Particularly during steady burn we found emission factors 4-7 times higher than those reported by Zai et
24 al.. This could be due to the use of a nephelometer by Zai et al. to assess mass concentrations.
25 Nephelometers have a very low response to the particles smaller than about 100 nm dominating emissions
26 during steady burn.

1
2 The mass emission factors for candle I during sooting burn in this study are similar to the results given by
3 Zai et al., while that of candle II is three times higher. On the other hand Fine et al. reported mass
4 emission factors close to the emission factor of candle II during sooting burn. EC is the dominant
5 component in both the present and Fine et al.'s study. It should be noted that EC emissions are a function
6 of the air velocity in the room and therefore very strong variations are expected under real-world
7 conditions. In previous reports (Zai et al. 2006 and Fine et al. 1999) no measurements of air-velocities
8 disturbing the flame during sooting burn were given, so a direct comparison is not possible to make.

9
10 Also during smouldering we found higher emission factors in this study compared to the Zai et al. study
11 (0.72 mg compared to 0.24 mg of particles emitted each time a candle is extinguished). Fine et al. (1999)
12 found similar emission factors to our data for a paraffin candle but more than two times higher for a
13 beeswax candle. Perhaps additives to the wick, such as flame retardants have an influence on the
14 smouldering time and emission levels.

15 16 **3.4 Detailed inorganic composition**

17 Emission factors were also derived using the box model for the inorganic components detected with Ion
18 Chromatography and PIXE. These are given in Table 3, the values are averaged for both sooting and
19 steady burn. It appeared that the composition of the ultrafine particles were similar in these two burning
20 modes. The compounds responsible for the high inorganic emissions from candle I are phosphates,
21 particularly of ammonium and to a lesser degree potassium. Very low metal emissions were found for
22 candle I. To identify the source of the phosphate particles, samples of wicks and wax were analyzed using
23 PIXE. We found a strong phosphorus signal from the wick of candle I, while phosphorus levels from the
24 wax were below the detection limit. Therefore we conclude that the ultrafine particles emitted from candle
25 I mainly consist of phosphates and that the source of these particles is additives to the wick, likely in the

1 form of ammonium phosphate added as a flame retardant to the wick. The molar ratio $\text{NH}_4^+/\text{PO}_4^{3-}$
2 calculated from the IC data was 1.15 ± 0.15 suggesting that the particles mainly consist of $\text{NH}_4\text{H}_2\text{PO}_4$.

3
4 For candle II, the main inorganic compounds detected were potassium, sodium and nitrate. Also several
5 metals were detected using PIXE. The main metal compounds detected were Cu, Sn and Co. These may
6 be from wick hardeners or from additives to the wax, such as color pigments. Candle II was a dark blue
7 candle, perhaps the detected Cu and Co originated from color pigments. Only Zn was detected with PIXE
8 at very low levels in the wick, while the other compounds were below the detection limit (Sn was not
9 analysed in the wick measurements), no compound was detected with PIXE in the wax. It is likely that the
10 metals occur in low concentrations in wax and/or wick and are strongly enriched in the fine particles.

11
12 When evaluating an ion balance using the detected compounds in the particle samples it becomes clear
13 that there are missing negative ions not analysed. Another very common flame retardant used in candle
14 wicks is BORAX™. BORAX mainly consists of sodium salts of boron, denoted borates. Neither PIXE,
15 nor the IC techniques used in this study allowed analysis of boron containing compounds. We conclude
16 that the ultrafine particles emitted during steady burn of candle II consist of nitrates of potassium and
17 sodium, metals and non-identified components not analyzed using IC and PIXE.

18
19 The observation that the composition of particle emissions from a combustion source can be dominated by
20 water-soluble salts during favourable combustion and that increasing quantities of OC/EC is added during
21 adverse combustion conditions is similar to that found in solid biofuel combustion (Wierzbicka et al.
22 2005, Pagels et al. 2003)

23
24 **3.5. On-line measurement of particle volatility**

25 Experiments with the TD placed upstream the SMPS enabled us to make indirect measurements of the
26 composition of the ultrafine particles while still airborne. The decrease in particle (effective) volume as a

1 function of heater temperature is given in Figure 7. It can be seen that ultrafine particles from candle I are
2 effectively evaporated at around 150 °C and that the remaining particles have a volume less than 5% of
3 the original particle. This is in agreement with particles from candle I being almost pure ammonium
4 phosphate. Di-ammonium-phosphate, $(\text{NH}_4)_2\text{HPO}_4$ decomposes at 155 °C (Lide, 2008).

5
6 A completely different volatility spectra was found for ultrafine particles from candle II. These particles
7 were only marginally affected at temperatures below 350 °C. But a strong decrease in particle volume was
8 found between 350 and 425 °C. Potassium nitrate decomposes at 400 °C (Lide, 2008), which is in
9 excellent agreement with the identified volatility. The remaining volume at 425 °C could be metal
10 compounds or non-analysed components, such as compounds containing boron. The slight decrease below
11 100 °C may be water bound as crystal water, but could also represent small amounts of organic carbon or
12 a more volatile salt such as ammonium nitrate.

13
14 Elemental carbon is non-volatile at temperatures up to at least 550 °C, while organic carbon is mainly
15 volatile below 100-150 °C. These data therefore ensure that the fraction of EC in ultrafine particles from
16 candle I is negligible and that the fraction of OC at least in candle II is low. In the analysis only particles
17 below 150 nm were included, thus excluding any interference with particles in the larger soot mode.
18 Similar measurements were also performed during sooting burn. It was found that the volatilities and
19 thereby the composition of the ultrafine particles was similar to the steady burn experiments, thus even
20 during sooting burn the composition of the ultrafine particles is mainly inorganic and EC/soot is almost
21 entirely emitted as larger particles. These measurements allowed us to verify the composition of the
22 ultrafine particles through measurements on gasborne particles, excluding uncertainties in filter
23 measurements such as evaporation and gas phase adsorption.

24
25 Another aim of using the Volatility-SMPS system was to ensure that the two candles brands studied here
26 were representative. A screening study was performed using eight different candle brands. Three of these

1 emitted ultrafine particles with volatilities similar to candle I and five with volatilities similar to candle II.
2 The size distributions (without TD) from these eight candles were also qualitatively similar to that of
3 candle I and II. Using the SMPS and the V-SMPS we could therefore, without the need to wait for time-
4 consuming chemical analysis, ensure that both in terms of number concentration, size and composition the
5 selected candles were representative of candles sold in Scandinavia.

6

7 **3.6. Chemically resolved particle size distribution**

8 Samples for size resolved chemical composition analysis were collected using the SDI-Impactor and
9 analysed using PIXE. The results are given in Figure 8. The impactor fractionates the mass concentration
10 into twelve stages according to the aerodynamic equivalent diameter rather than the mobility diameter,
11 which is determined by the SMPS. The only components detected above the detection limit in more than
12 one impactor stage for candle I were phosphorus and potassium (only elements with atomic numbers
13 larger than 12 can be detected with PIXE, so carbon, nitrogen and sodium for example can not be
14 detected). These two components (P and K) have similar size distribution and virtually all emissions occur
15 at sizes below 1 μm , as expected for an aerosol generated through evaporation followed by condensation.
16 For candle II the only detected components in the impactor measurements were potassium, tin and copper,
17 also in this case virtually all detected mass was below 1 μm . The size distribution is similar for potassium
18 and the metals. This suggests that heavy metals emitted from candles occur to a large extent in the same
19 particles as the continuously emitted inorganic ultrafine particles and are perhaps to a lesser degree
20 associated with the larger soot and organics dominated particles emitted during sooting burn and
21 smouldering.

22

23 **3.7. Mass closure of SMPS, TEOM and filter measurements**

24 The data reduction procedure to calculate mass concentrations and mass size distributions is illustrated in
25 Figures 9 and 10 for an example of an experiment involving candle II during steady burn. First the
26 experimental “effective” volume distribution is determined by weighing the number size distribution by

1 volume. Then three lognormal size modes are fitted to the effective volume distribution using the least-
2 squares fitting procedure. Two modes need to be used for the ultrafine particles since a smaller mode of
3 freshly produced particles and a larger mode of particles formed by self-coagulation occur. For the soot
4 particles a single mode is sufficient. It can be seen in Figure 9 that a satisfactory fit to the experimental
5 data can be obtained using these three lognormal modes.

6
7 To generate the mass size distribution, the effective density of particles in each mode needs to be known.
8 We used a combination of empirical data from the literature and this study. Effective density data from
9 Park et al. (2003) for diesel soot was used for the soot mode. A fractal dimension of 2.4 and an effective
10 density which equals $0.4 \times 10^3 \text{ kg m}^{-3}$ at 300 nm was used. Using a fractal dimension smaller than 3.0
11 leads to a decreasing effective density with increasing particle size.

12
13 The effective density was assumed to be the same for the two ultrafine modes with a constant value for all
14 particle diameters. We performed a few Hygroscopic Tandem DMA measurements which showed that the
15 ultrafine particles from candles contain 10-15% water and are therefore likely to be spherical or at least
16 compact liquid droplets at the 30% RH used in the chamber. This would inhibit any agglomerate
17 formation, suggesting that a size-independent effective density may be suitable.

18
19 The effective density of the soot mode was held fixed according to the values by Park et al. (2003). The
20 effective density of the ultrafine modes was then varied, until the best fit of the total mass concentration
21 from the SMPS agreed with the mass concentration of the TEOM. The fitted values for the ultrafine
22 particle modes were $1.6 \pm 0.2 \times 10^3 \text{ kg m}^{-3}$ for candle I and $1.5 \pm 0.2 \times 10^3 \text{ kg m}^{-3}$ for candle II. This is
23 lower than the bulk densities of the compounds making up the particles (mono-ammonium phosphate has
24 a density of $1.8 \times 10^3 \text{ kg m}^{-3}$ and potassium nitrate has a density of $2.1 \times 10^3 \text{ kg m}^{-3}$), (Lide, 2008). When
25 these values are known, the mass size distribution can be determined as illustrated in Figure 10. The low
26 effective density of soot (below $0.3 \times 10^3 \text{ kg m}^{-3}$ near the mass distribution peak at 600 nm) reduces the

1 magnitude of the soot mode compared to the ultrafine modes when going from the effective volume
2 distribution (Figure 9) to the mass size distribution (Figure 10). Effective volume distributions or mass
3 distributions, where a constant effective density of $1.0 \times 10^3 \text{ kg m}^{-3}$ is assumed are often used in the
4 literature to estimate volume or mass concentrations. It should be noted that the volume or mass
5 concentration of soot agglomerates from candles are over-estimated by more than a factor of three using
6 such approaches.

7
8 To determine the effective density of the organic particles from smouldering, first the fitted density of the
9 ultrafine particles from the steady burn experiments was used for the ultrafine modes. Then the effective
10 density of the larger OC dominated mode was fitted to be $1.1 \pm 0.2 \times 10^3 \text{ kg m}^{-3}$, which is slightly higher
11 than the value for pure paraffin and stearic acid (around $0.9 \times 10^3 \text{ kg m}^{-3}$).

12
13 In Figure 11 the three different methods to determine the total mass concentration are compared. The
14 methods consisted of: 1) the mass concentration from the TEOM, 2) the size-integrated SMPS mass
15 concentration and 3) filter mass concentration obtained by adding the concentrations of EC, organics and
16 all inorganics detected with PIXE and IC. It can be seen that the total concentration of the three methods is
17 in most cases within 25%, which has to be considered satisfactory. Slightly larger differences were found
18 between filter and TEOM measurements during steady burn of candle II. Presumably due to low
19 concentrations collected onto the filters. Given are also mass concentrations of the three major classes of
20 chemical compounds and ultrafine and fine modes fitted to the SMPS data. It can be seen that the
21 agreement between the concentration of Filter-EC and the fine mode is good in “sooting burn”
22 experiments. Thus the effective density for fractal-like diesel soot particles can be used to accurately
23 describe the mass-mobility relationship of candle soot, even though the candle soot agglomerates are
24 larger than diesel soot.

25

1 The agreement between organics and the fine mode is satisfactory during smouldering experiments. The
2 inorganic concentration is slightly higher than the SMPS-ultrafine mode, the reason for this is not clear.
3 The discrepancy was larger during sooting burn. Perhaps this is due to some inorganics being transferred
4 to the soot mode through coagulation. As shown by Pagels et al. (2008) soot particles retain their complex
5 morphology when modest additional material is transferred to the particles as the particles age. This is
6 reflected by the low effective density and complex morphology of the candle soot.

7

8 **4 Conclusions - implications and recommendation for manufacturers and users**

9 The large differences in composition, particle size and effective density between the different modes in the
10 particle size distribution of candle emissions illustrate that distinctly different particle types are emitted
11 during the different modes of candle burning. This has important implications for potential adverse health
12 effects.

13

14 Candles emit ultrafine particles resulting in comparatively high number concentrations in indoor air and
15 these particles mainly consist of inorganic salts. The water-soluble nature of ammonium phosphate and
16 alkali nitrates dominating the composition of the ultrafine particles is an important observation. There are
17 suggestions that the number or surface area concentration of *insoluble* fine particles may be a more
18 relevant dose metric than particle mass (Maynard 2001). The number concentration of ultrafine particles
19 from candles is very high. However, the mass emission factors (which for soluble particles may be the
20 most relevant dose metric) associated with the ultrafine mode is only moderate. Thus potential adverse
21 health effects of particles emitted from steady burning candles may be less than expected from number
22 concentration measurements.

23

24 Another implication of the water-soluble nature of these combustion particles is that they grow due to
25 water-uptake in the humid respiratory tract (Rissler et al. 2005), thus decreasing the diffusion coefficient
26 and the deposition probability. For example, hygroscopic NaCl particles of 30 nm have a more than two

1 times lower deposition probability in the respiratory tract compared to hydrophobic oil particles of the
2 same dry size (Löndahl et al. 2007). However, as shown for candle II in this study, these ultrafine particles
3 may contain metals. Metals have been suggested to be mediators of adverse health effects associated with
4 ultrafine particles. Measurements of both total number concentrations and metal content is strongly
5 recommended to manufacturers. By choosing alternative flame retardants and other additives it may be
6 possible to strongly decrease both the number and mass emission factors during steady burn.

7
8 During sooting burn, candles emit relatively high levels of elemental carbon (EC). Candle soot show
9 similarities to diesel soot in terms of morphology. One important difference is that diesel soot often
10 contains a substantial fraction of condensed organic carbon, of which some may be important for adverse
11 health effects, for example Poly Aromatic Hydrocarbons (PAHs). Lau et al. (1997) found comparatively
12 low PAH emissions from candles. However, a more detailed study of PAH emissions also needs to be
13 done during strongly sooting conditions. Another difference between candle soot and diesel soot is that
14 candle soot agglomerates have substantially larger mobility diameters and therefore a lower deposition
15 probability in the respiratory tract. It should be noted that present deposition models assume spherical
16 particles and have not been validated for highly agglomerated soot particles. Hygroscopic material can be
17 transferred to the soot through coagulation in indoor air. Condensed hygroscopic material can transform
18 the particles to more compact forms within the respiratory tract due to uptake of water (Zhang et al. 2008).
19 There is a strong need to establish relevant and meaningful industry standards for EC emission
20 measurements from candles using relevant convective air flows, similar to that what might occur in real
21 indoor settings. For example in the future it may be plausible that candles are labeled with a “sooting
22 index”.

23
24 The magnitude of soot exposures from candles is poorly known today. Therefore there is a need for field
25 measurements of EC associated with candle emissions. The magnitude of soot emissions is strongly
26 dependent on the convective air flow patterns in indoor air. Some studies suggest that candles can make a

1 relatively strong contribution to the personal exposure to EC (Sorensen et al. 2005, Ogden et al. 2000). It
2 should be pointed out that most soot emissions from candles can be avoided by using high-quality candles,
3 trimming long wicks and by avoiding burning candles when air flows are so high that the candle flame
4 flickers or even visible soot plumes appear.

5

6 **Acknowledgements:** The work was supported by the Swedish research council FORMAS and SBUF, The
7 construction industry's organisation for research and development

8

1 **References**

- 2 Afshari,A., Matson,U., Ekberg,L.E., 2005. Characterization of indoor sources of fine and ultrafine particles: a study
3 conducted in a full-scale chamber, *Indoor Air* 15, pp. 141-150.
- 4 Burtscher,H., Baltensperger,U., Bukowiecki,N., Cohn,P., Hüglin,C., Mohr,M., Matter,U., Nyeki,S., Schmatloch,V.,
5 Streit,N., Weingartner,E., 2001. Separation of volatile and non-volatile aerosol fractions by thermodesorption:
6 instrumental development and applications, *Journal of Aerosol Science* 32, pp. 427-442.
- 7 Chow,J.C., Watson,J.G., Pritchett,L.C., Pierson,W.R., Frazier,C.A., Purcell,R.G., 1993. The Dri Thermal Optical
8 Reflectance Carbon Analysis System - Description, Evaluation and Applications in United-States Air-Quality
9 Studies, *Atmospheric Environment Part A-General Topics* 27, pp. 1185-1201.
- 10 Edwards,H.G.M., Farwell,D.W., Brooke,C.J., 2005. Raman spectroscopic study of a post-medieval wall painting in
11 need of conservation, *Analytical and Bioanalytical Chemistry* 383, pp. 312-321.
- 12 Fan,C.W., Zhang,J.J., 2001. Characterization of emissions from portable household combustion devices: particle size
13 distributions, emission rates and factors, and potential exposures, *Atmospheric Environment* 35, pp. 1281-1290.
- 14 Fine,P.M., Cass,G.R., Simoneit,B.R.T., 1999. Characterization of fine particle emissions from burning church
15 candles, *Environmental Science & Technology* 33, pp. 2352-2362.
- 16 Heidam,N.Z., 1981. Review - Aerosol Fractionation by Sequential Filtration with Nuclepore Filters, *Atmospheric*
17 *Environment* 15, pp. 891-904.
- 18 Hussein,T., Glytsos,T., Ondracek,J., Dohanyosova,P., Zdimal,V., Hameri,K., Lazaridis,M., Smolik,J., Kulmala,M.,
19 2006. Particle size characterization and emission rates during indoor activities in a house, *Atmospheric*
20 *Environment* 40, pp. 4285-4307.
- 21 Huynh,C.K., Savolainen,H., Vuduc,T., Guillemin,M., Iselin,F., 1991. Impact of Thermal Proofing of A Church on
22 Its Indoor Air-Quality - the Combustion of Candles and Incense As A Source of Pollution, *Science of the Total*
23 *Environment* 102, pp. 241-251.
- 24 Klepeis,N.E., Nelson,W.C., Ott,W.R., Robinson,J.P., Tsang,A.M., Switzer,P., Behar,J.V., Hern,S.C.,
25 Engelmann,W.H., 2001. The National Human Activity Pattern Survey (NHAPS): a resource for assessing
26 exposure to environmental pollutants, *Journal of Exposure Analysis and Environmental Epidemiology* 11, pp.
27 231-252.

1 Knight,L., Levin,A., Mendenhall C., 2001. Candles and Incense as potential sources of indoor air pollution: market
2 analysis and literature review, *United States Environmental Protection Agency*, National Risk Management
3 Research Laboratory Cincinnati, Ohio 45268.

4 Koutrakis,P., Brauer,M., Briggs,S.L.K., Leaderer,B.P., 1991. Indoor Exposures to Fine Aerosols and Acid Gases,
5 *Environmental Health Perspectives* 95, pp. 23-28.

6 Larosa,L.B., Buckley,T.J., Wallace,L.A., 2002. Real-time indoor and outdoor measurements of black carbon in an
7 occupied house: An examination of sources, *Journal of the Air & Waste Management Association* 52, pp. 41-49.

8 Lau,C., Fiedler,H., Hutzinger,O., Schwind,K.H., Hosseinpour,J., 1997. Levels of selected organic compounds in
9 materials for candle production and human exposure to candle emissions, *Chemosphere* 34, pp. 1623-1630.

10 Li,W., Hopke,P.K., 1993. Initial Size Distributions and Hygroscopicity of Indoor Combustion Aerosol-Particles,
11 *Aerosol Science and Technology* 19, pp. 305-316.

12 Lide,D.R., ed., 2008. CRC Handbook of Chemistry and Physics, 88th Edition (Internet Version 2008), CRC
13 Press/Taylor and Francis, Boca Raton, FL, USA.

14 Lin,T.S., Shen,F.M., Chen,J.L., Yang,M.H., 2003. Trace metals in candle smoke, *Bulletin of Environmental*
15 *Contamination and Toxicology* 70, pp. 182-187.

16 Londahl,J., Massling,A., Pagels,J., Swietlicki,E., Vaclavik,E., Loft,S., 2007. Size-resolved respiratory-tract
17 deposition of fine and ultrafine hydrophobic and hygroscopic aerosol particles during rest and exercise, *Inhalation*
18 *Toxicology* 19, pp. 109-116.

19 Long,C.M., Suh,H.H., Koutrakis,P., 2000. Characterization of indoor particle sources using continuous mass and
20 size monitors, *Journal of the Air & Waste Management Association* 50, pp. 1236-1250.

21 Martinsson,B.G., Karlsson,M.N.A., Frank,G., 2001. Methodology to estimate the transfer function of individual
22 differential mobility analyzers, *Aerosol Science and Technology* 35, pp. 815-823.

23 Matson,U., 2005. Indoor and outdoor concentrations of ultrafine particles in some Scandinavian rural and urban
24 areas, *Science of the Total Environment* 343, pp. 169-176.

25 Maynard,A.D., Maynard,R.L., 2002. A derived association between ambient aerosol surface area and excess
26 mortality using historic time series data, *Atmospheric Environment* 36, pp. 5561-5567.

27 Nriagu,J.O., Kim,M.J., 2000. Emissions of lead and zinc from candles with metal-core wicks, *Science of the Total*
28 *Environment* 250, pp. 37-41.

1 Ogulei,D., Hopke,P.K., Wallace,L.A., 2006. Analysis of indoor particle size distributions in an occupied townhouse
2 using positive matrix factorization, *Indoor Air* 16, pp. 204-215.

3 Pagels,J., Strand,M., Rissler,J., Szpila,A., Gudmundsson,A., Bohgard,M., Lillieblad,L., Sanati,M., Swietlicki,E.,
4 2003. Characteristics of aerosol particles formed during grate combustion of moist forest residue. *Journal of*
5 *Aerosol Science* 34, pp. 1043-1059.

6 Pagels J., Khalizov A., McMurry PH. and Zhang RY., (2008) Processing of Soot by Controlled Sulphuric Acid and
7 Water Condensation – Mass and Mobility Relationship. Accepted for publication in *Aerosol Science and*
8 *Technology*.

9 Park,K., Cao,F., Kittelson,D.B., McMurry,P.H., 2003. Relationship between particle mass and mobility for diesel
10 exhaust particles, *Environmental Science & Technology* 37, pp. 577-583.

11 Park,K., Kittelson,D.B., McMurry,P.H., 2004. Structural properties of diesel exhaust particles measured by
12 transmission electron microscopy (TEM): Relationships to particle mass and mobility, *Aerosol Science and*
13 *Technology* 38, pp. 881-889.

14 Perez,F.R., Edwards,H.G.M., Rivas,A., Drummond,L., 1999. Fourier transform Raman spectroscopic
15 characterization of pigments in the mediaeval frescoes at Convento de la Peregrina, Sahagun, Leon, Spain. Part 1 -
16 Preliminary study, *Journal of Raman Spectroscopy* 30, p. 301-+.

17 Rissler,J., Pagels,J., Swietlicki,E., Wierzbicka,A., Strand,M., Lillieblad,L., Sanati,M., Bohgard,M., 2005.
18 Hygroscopic behavior of aerosol particles emitted from biomass fired grate boilers, *Aerosol Science and*
19 *Technology* 39, pp. 919-930.

20 Sakurai,H., Park,K., McMurry,P.H., Zarling,D.D., Kittelson,D.B., Ziemann,P.J., 2003. Size-dependent mixing
21 characteristics of volatile and nonvolatile components in diesel exhaust aerosols, *Environmental Science &*
22 *Technology* 37, pp. 5487-5495.

23 Sorensen,M., Loft,S., Andersen,H.V., Nielsen,O.R., Skovgaard,L.T., Knudsen,L.E., Ivan,V.N.B., Hertel,O., 2005.
24 Personal exposure to PM_{2.5}, black smoke and NO₂ in Copenhagen: relationship to bedroom and outdoor
25 concentrations covering seasonal variation, *Journal of Exposure Analysis and Environmental Epidemiology* 15,
26 pp. 413-422.

27 Zai. S., Huang,Z., Wang,J.S., 2006. Studies on the size distribution, number and mass emission factors of candle
28 particles characterized by modes of burning, *Journal of Aerosol Science* 37, pp. 1484-1496.

1 van Alphen,M., 1999. Emission testing and inhalational exposure-based risk assessment for candles having Pb metal
2 wick cores, *Science of the Total Environment* 244, pp. 53-65.

3 Wasson,S.J., Guo,Z.S., McBrian,J.A., Beach,L.O., 2002. Lead in candle emissions, *Science of the Total Environment*
4 296, pp. 159-174.

5 Wierzbicka,A., Lillieblad,L., Pagels,J., Strand,M., Gudmundsson,A., Gharibi,A., Swietlicki,E., Sanati,M.,
6 Bohgard,M., 2005. Particle emissions from district heating units operating on three commonly used biofuels,
7 *Atmospheric Environment* 39, pp. 139-150.

8 Wierzbicka A., Gudmundsson A., Pagels J., Dahl A., Löndahl J., Swietlicki E. and Bohgard M. 2008. Characteristics
9 of Airborne Particles in Various Swedish Indoor Environments. Paper I in *What Are the Characteristics of*
10 *Airborne Particles that We Are Exposed to? Focus on Indoor Environments and Emissions from Biomass Fired*
11 *District Heating*, PhD Thesis, Lund University 2008

12 Zhang RY., Khalizov AF., Pagels J., Zhang DD., Xue H., J. Chen and McMurry PH. (2008) Variability in
13 morphology, hygroscopicity and optical properties of soot aerosols during internal mixing in the atmosphere.
14 *Proceedings of the National Academy of Sciences of the United States of America.* 30: 10291-10296

15

FIGURE CAPTIONS

- 1
- 2 Figure 1. Schematic figure of experimental set-up
- 3
- 4 Figure 2. Average number particle size distributions in the 21.6 m³ chamber during steady and sooting
- 5 burn of 4 candles. Air exchange rate was 0.5 h⁻¹.
- 6
- 7 Figure 3. Influence of smouldering emissions upon candle extinction on the particle number size
- 8 distribution. Four candles of type II were burning for 10 min before extinguishing. Average of three
- 9 repeated experiments. The air exchange rate was 0.5 h⁻¹.
- 10
- 11 Figure 4. TEM images of particles in the soot mode at different magnification. Candle II, “sooting”
- 12 combustion.
- 13
- 14 Figure 5. Chemical composition of candle smoke for the two candle types at different burning conditions,
- 15 given as average mass concentration in the chamber over a period of 60 minutes after the candle is either
- 16 lighted (sooting and steady burn) or extinguished (smoulder). Note that the EC - concentration during
- 17 sooting burn for candle II extends out of scale and the value is 1424 µg/m³.
- 18
- 19 Figure 6. Experimental and modeled mass concentrations in the chamber during a steady burn experiment
- 20 for candle II, TEOM data (PM2.5). The modeled concentration and fitted emission factor was obtained
- 21 using the least squares optimization procedure. Wall losses were modeled in two different ways, 1. using
- 22 the average GMD of the whole experiment to estimate losses or 2. using the GMD of each SMPS scan
- 23 (time dependent losses).
- 24
- 25 Figure. 7. The remaining volume fraction as a function of temperature. A thermodesorber was used
- 26 upstream the SMPS, “Steady Burn” experiments.

1
2 Figure 8. Aerodynamic particle size distribution of major elements detected in steady burn experiments
3 with four candles burning in the chamber. Left: Candle I, Right: Candle II. Samples collected with the SDI
4 impactor and analyzed using PIXE.

5
6 Figure 9. “Effective” volume distribution, with three fitted lognormal modes. Example for Candle II,
7 steady burn.

8
9 Figure 10. Assessed mass distribution of SMPS measurements, with three fitted lognormal modes.
10 Example for Candle II during steady burn. An effective density of $1.5 \times 10^3 \text{ kg m}^{-3}$ was used for the two
11 ultrafine modes and a size dependent effective density used for the “soot” mode (Park et al. 2003).

12
13 Figure 11. Comparison of mass concentrations obtained from TEOM, filter and SMPS. For SMPS
14 measurements the empirically determined effective densities were used. Measurements during sooting
15 burn of candle II were multiplied by 0.5 to fit the scale.

16

TABLE

Table 1. Summary of deduced emission factors of candle smoke particles (for a single candle). Comparisons to literature data. Uncertainties given as standard deviations of repeated measurements. PM2.5 mass measured independently using the TEOM.

Candle Type – Burn Mode	Reference	PM2.5 mass (mg h ⁻¹)	Elemental Carbon (mg h ⁻¹)	Organic Matter (mg h ⁻¹)	Inorganic Compounds (mg h ⁻¹)
Candle I – Steady Burn	This study	2.4 ± 0.1	0.14 ± 0.11	0.04 ± 0.06	2.9 ± 0.5
Candle II – Steady Burn	This study	0.87 ± 0.14	0.31 ± 0.36	0.05 ± 0.07	0.92 ± 0.34
Paraffin candle - Steady Burn	Zai et al. 2006	0.33 ± 0.03	-	-	-
Candle I – Sooting	This study	8.9 ± 0.4	4.5 ± 0.2	0.24 ± 0.33	3.3 ± 0.6
Candle II – Sooting	This study	25.3 ± 0.02	19.0 ± 0.6	1.3 ± 0.3	1.1 ± 0.6
Paraffin candle - Sooting	Fine et al. 1999	26.6	24.1	1.4	-
Paraffin candle - Sooting	Zai et al. 2006	7.6 ± 2.2	-	-	-

Table 2. Summary of deduced emission factors of candle smoke particles. Smouldering emissions given as mg particles released upon a single extinction of a single candle, comparisons to literature data. Uncertainties given as standard deviations of repeated measurements.

Candle Type – Burn Mode	Reference	PM2.5 mass (mg)	Elemental Carbon (mg)	Organic Matter (mg)	Inorganic Compounds (mg)
Candle II – Smoulder	This study	0.72 ± 0.04	0.03 ± 0.01	0.80 ± 0.03	0.11 ± 0.06
Paraffin candle - Smoulder	Fine et al. 1999	0.65 ± 0.14	0.05 ± 0.05	0.82 ± 0.19	-
Beeswax candle – Smoulder	Fine et al. 1999	1.7 ± 0.35	<0.04	1.9 ± 0.36	-
Paraffin candle - Smoulder	Zai et al. 2006	0.24 ± 0.07	-	-	-

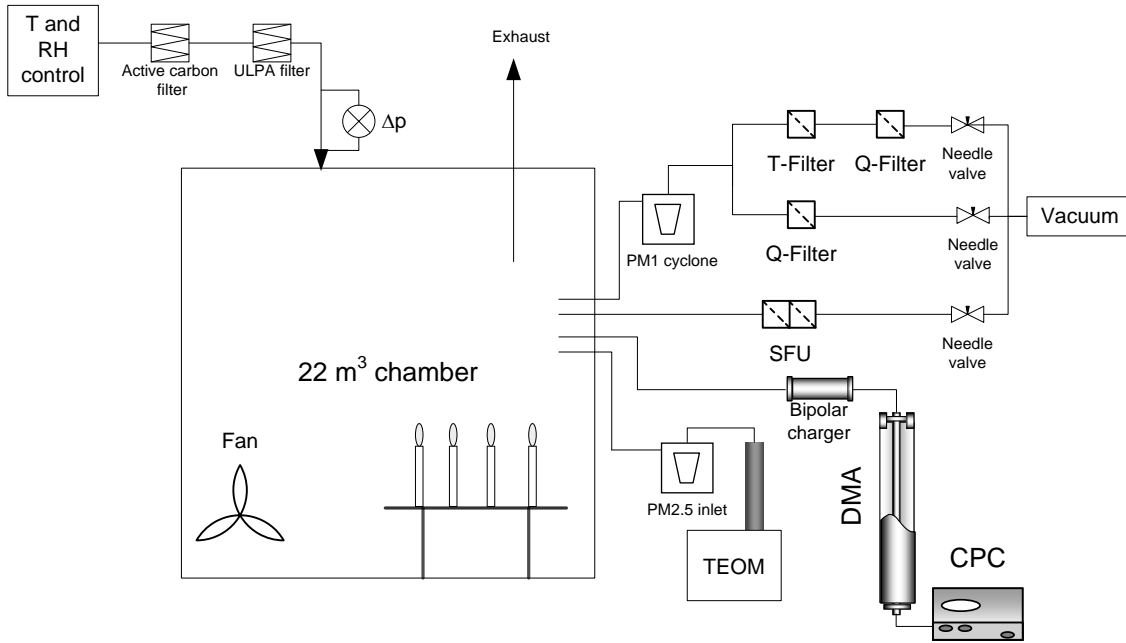
1 Table 3. Detailed inorganic composition for candle I and II from PIXE (n=2) and IC (n=3) analysis, given
2 as emission factors ($\mu\text{g h}^{-1}$) for each component. Average of steady and sooting burn experiments for each
3 candle.

4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31

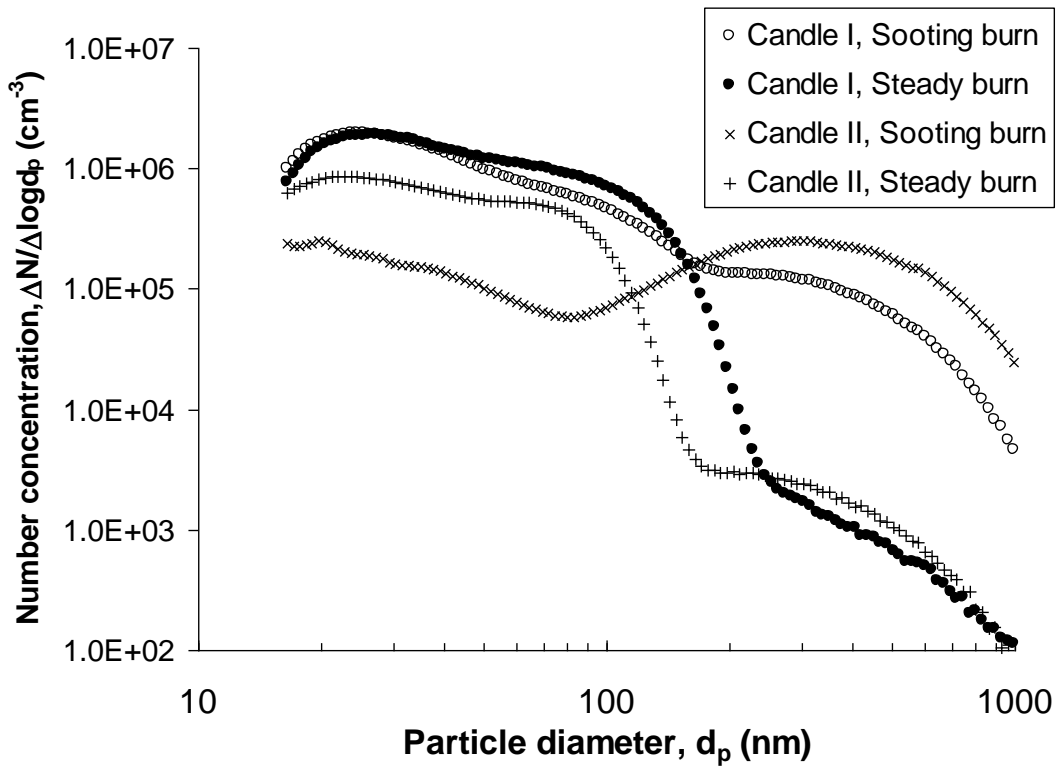
	Candle I	Candle II
PO₄³⁻	2300	1
NO₃⁻	20	310
SO₄²⁻	9	5
Cl⁻	28	47
F⁻	20	23
NH₄⁺	490	17
Na⁺	45	210
K⁺	140	270
Cu	0	80
Sn	1	44
Co	0	19
Zn	0	2
Pb	0	3
Sum	3060	1030

1

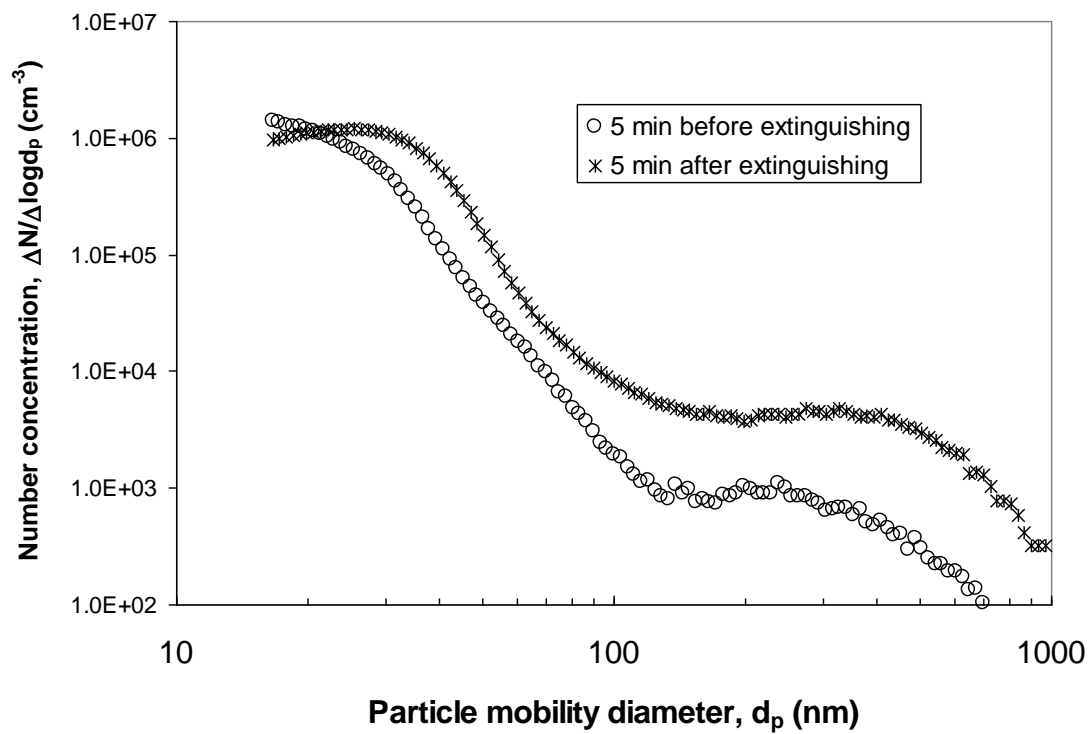
FIGURES



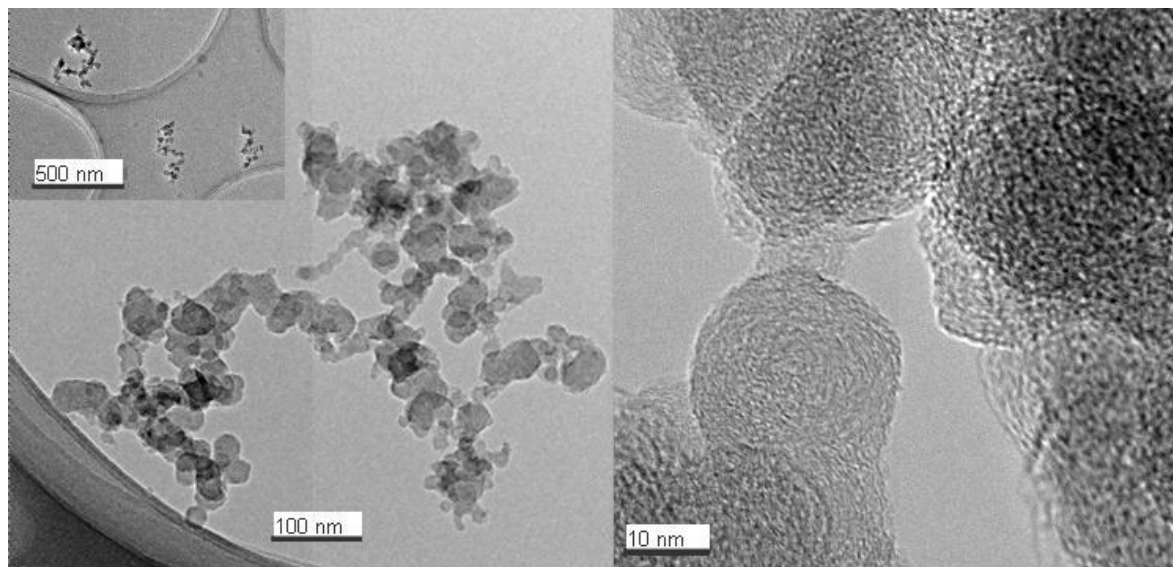
2
3
4
5
Figure 1.



6
7
8
Figure 2.



1
2
3
4
5
Figure 3.



6
7
8
Figure 4.

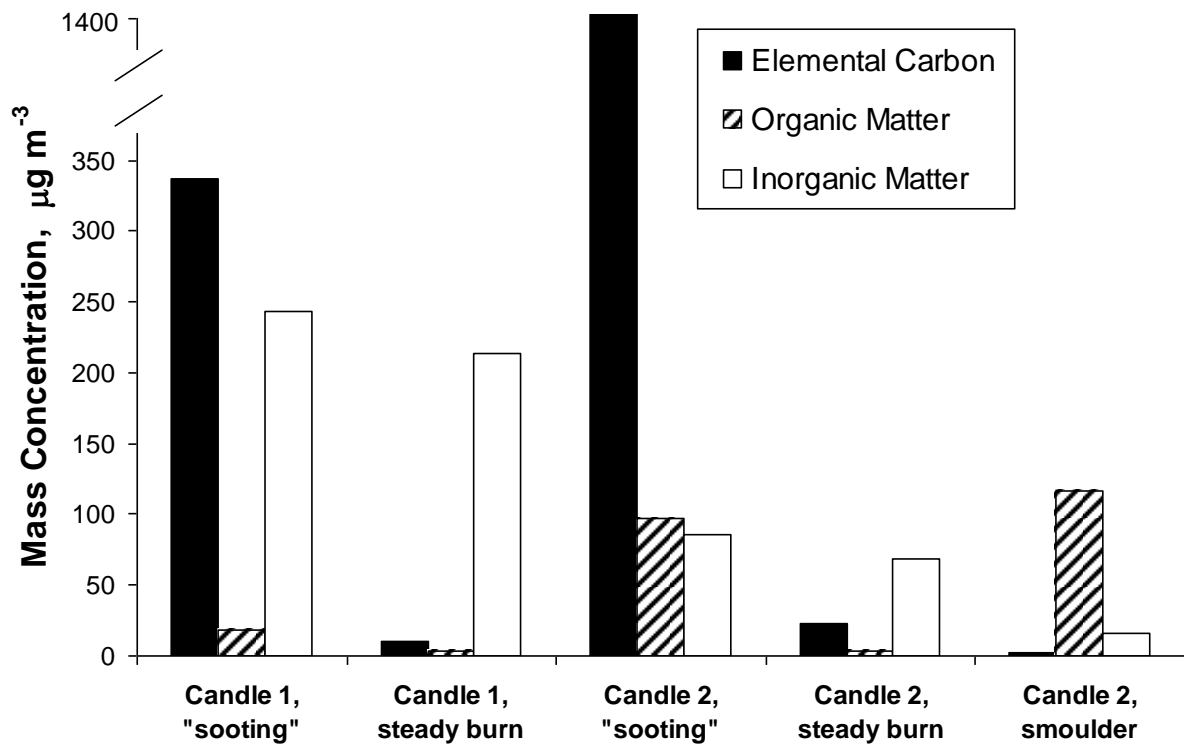


Figure 5.

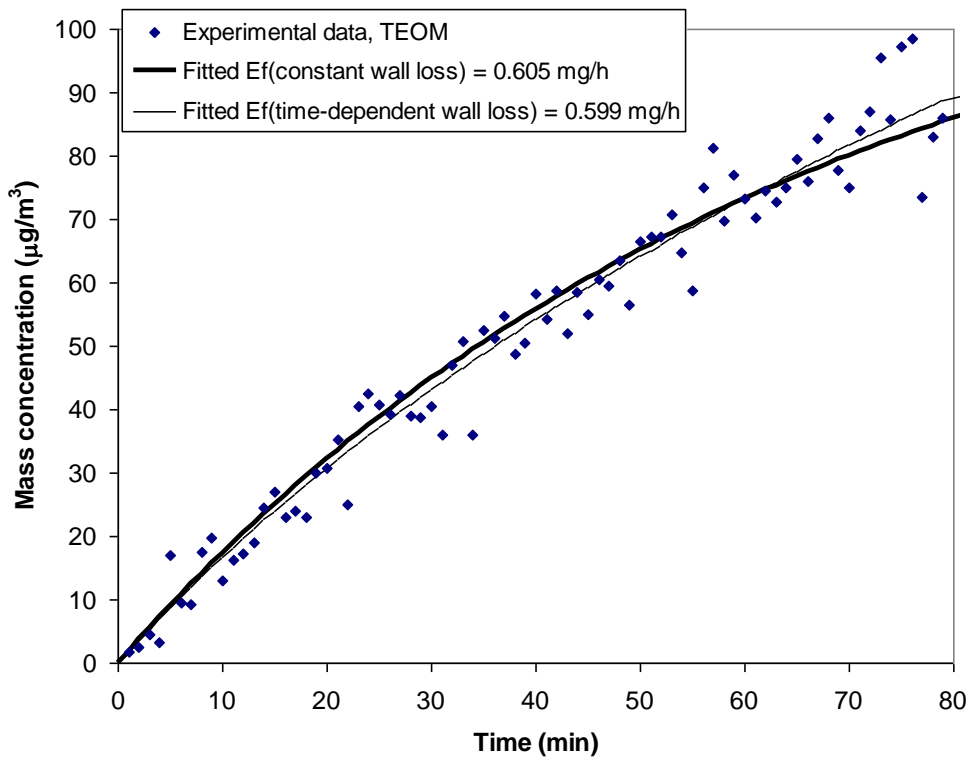


Figure 6

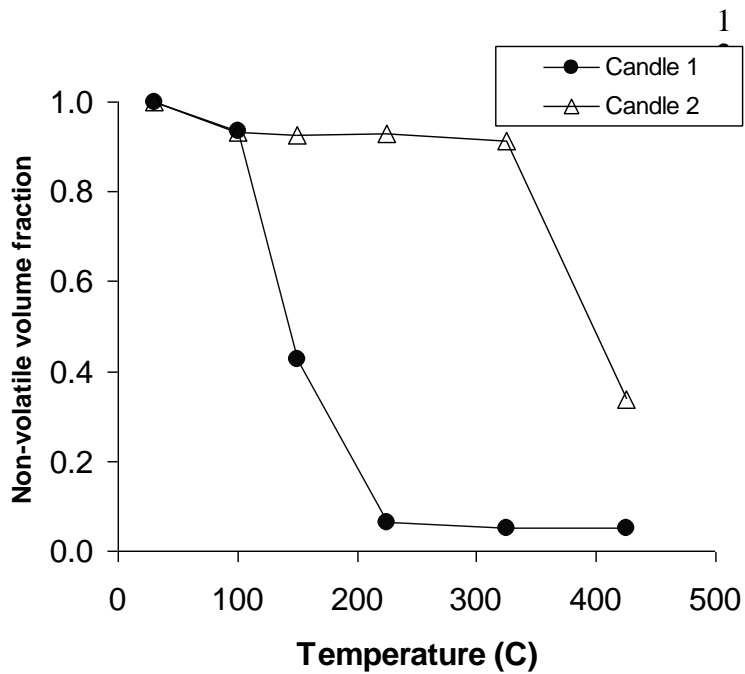


Figure 7.

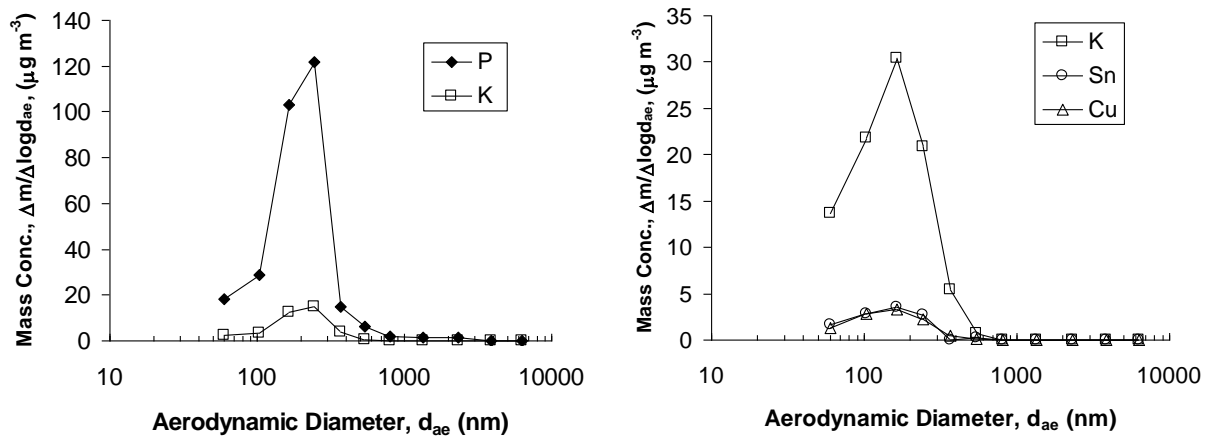
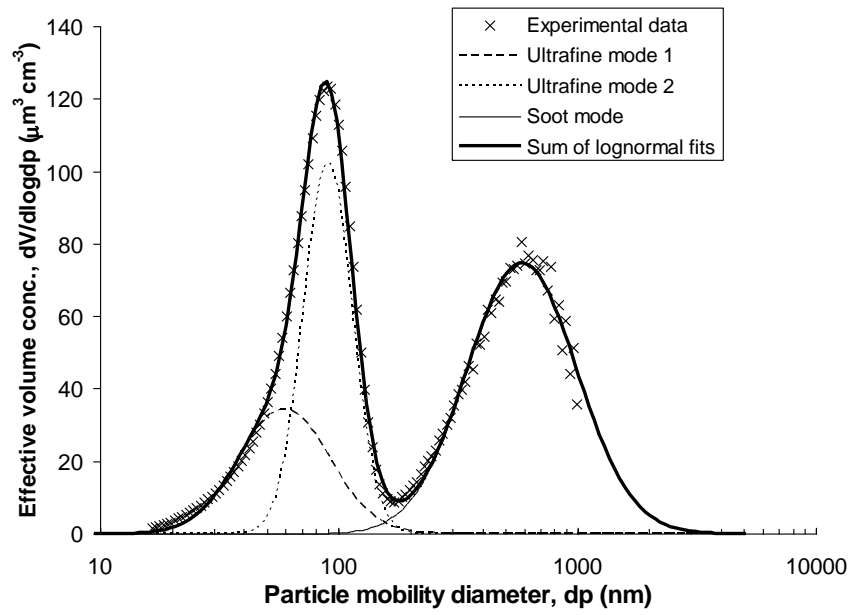
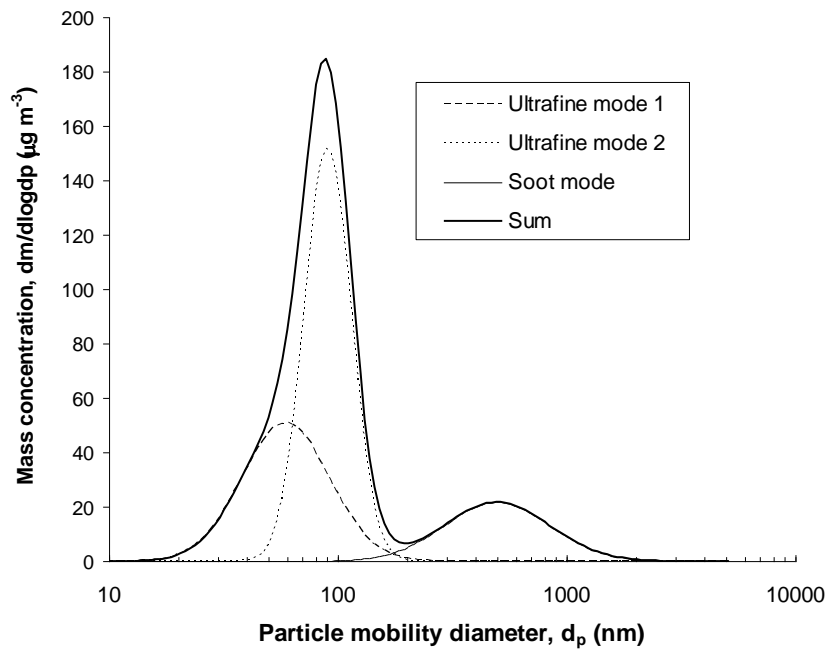


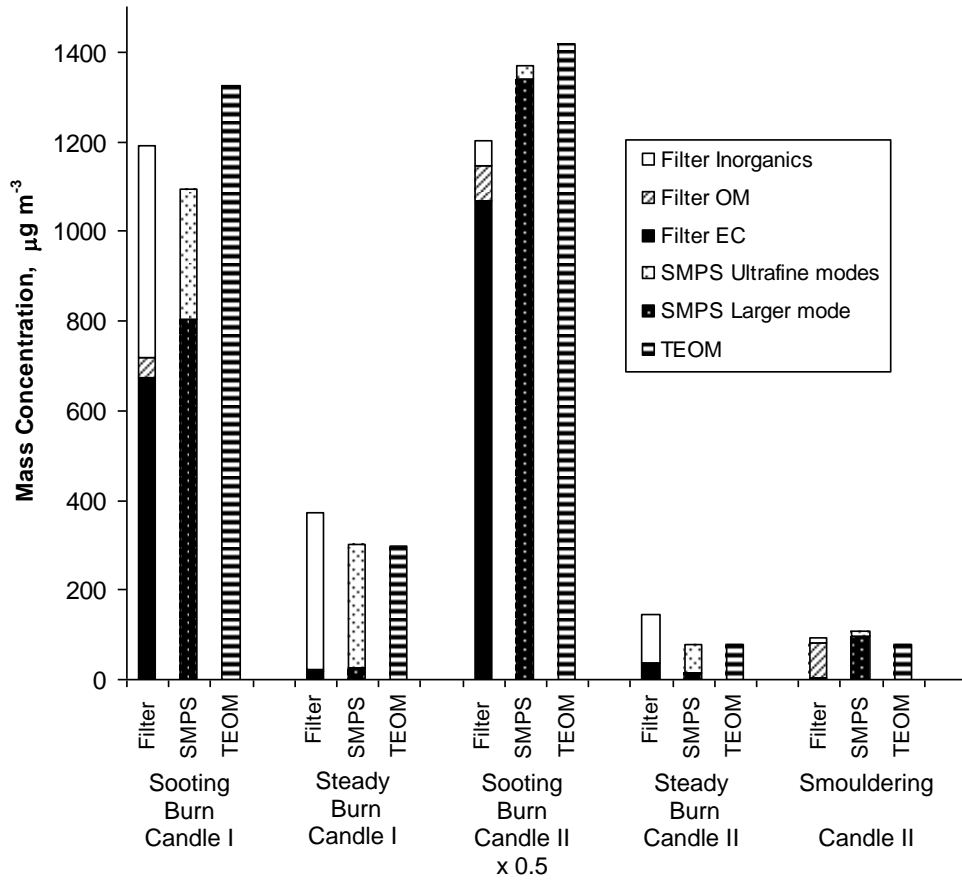
Figure 8.



1
2 Figure 9.



3
4 Figure 10.
5



1
2
3
Figure 11.