



Technical Note

Characterisation of a Commercially Available Thermodenuder and Diffusion Drier for Ultrafine Particles Losses

Svetlana Stevanovic^{1*}, Branka Miljevic¹, Pierre Madl², Samuel Clifford¹, Zoran Ristovski¹

¹ *International Laboratory for Air Quality and Health, Queensland University of Technology, Australia*

² *Department of Molecular Biology, Division of Physics and Biophysics, University of Salzburg, A-5020 Salzburg, Austria*

ABSTRACT

Volatility of particles is an important physical property and it directly influences the chemical composition of aerosols and thus their reactivity and related toxicity. Thermodenuders (TD) are widely used for the volatility studies, which is primarily giving an insight into the kinetics of evaporation and condensation within the device. In addition, characterisation of particle phase component depends on the humidity of the carrier gas and the presence of semi volatile organic compounds. Diffusion dryers are most commonly used for the removal of gas phase and volatile organic compounds and water vapour. The interpretation of data when using thermodenuders and diffusion dryers often excludes the correction factors that describe particle losses inside these instruments. To address this deficiency a commercially available TD and diffusion drier were characterised in the laboratory. For the TD the temperature profiles inside the TD showed optimal results only within a very narrow flow-window of 1 L/min resulting in inhomogeneous profiles for the flow rates outside this range. Losses at ambient temperature were very high for particles smaller than 50 nm and were dependent on the particle composition with higher losses observed for sodium chloride particles (> 60%). As with TD particle losses for NaCl at room temperature, the biggest losses (15–50%) are for small particles with diameters smaller than 50 nm. The number losses for particles bigger than 65 nm are considerably smaller and they are much lower (~10%) for particles bigger than 0.1 µm. From the experimental results a logistic regression model is fitted to the size dependent loss function. This model should be used to correct for the losses especially if aerosols smaller than 50 nm are studied.

Keywords: Thermodenuder; Diffusion dryer; Particle losses; Volatility; Regression model.

INTRODUCTION

The importance of organics in particulate toxicity has been widely recognised (Mauderly and Chow, 2008). The volatility of organic aerosol (OA) is directly related to its chemical composition giving us insight into the possible oxidation pathways under atmospheric conditions (Jonsson *et al.*, 2007). The fraction that is believed to contribute the most to this particle related toxicity is the semi-volatile organic fraction. Depending on the source and atmospheric conditions the semi-volatile fraction can be significant portion of the aerosols in question (Robinson *et al.*, 2007). Volatility measurements have been widely performed for over a number of years (Kulmala *et al.*, 2000; Sakurai *et al.*, 2003a; Johnson *et al.*, 2004; Biswas *et al.*, 2007; Meyer and Ristovski, 2007). Thermodenuders (TDs) are the most commonly used instruments for near-real time measurement

of the volatile and non-volatile fraction, both in the field (Wehner *et al.*, 2002) and in the laboratory (An *et al.*, 2007; Jonsson *et al.*, 2007).

TDs are comprised of two sections - one for heating and one for cooling. They are designed to remove the volatile and semi-volatile fractions by thermal desorption. The volatile and semi-volatile fractions are heated to achieve complete evaporation and are trapped by adsorption on activated charcoal in the cooling section.

Proper measurement of the volatile fraction must include characterisation of the temperature profile, particle losses and gas adsorption efficiency in the thermodenuder. Characterising the temperature profile is important as temperature determines the residence time inside the TD as well as the efficiency of evaporation. Complete evaporation presumes uniform temperature in the heating part and an adequate residence time inside the cooling part. Burtscher *et al.* (2001) showed that sedimentation only influences the particle losses in the case of micron- sized particles. In the case of submicron particles, particle losses inside the TD are mainly caused by thermophoretic and diffusional processes. The amount of data collected with TDs is growing, but

* Corresponding author.

E-mail address: s.stevanovic@qut.edu.au

interpretation of the results is often performed without correcting for transport efficiency and losses.

As a great number of researchers use the commercially available TSI 3065 TD as a part of their experimental setup (Johnson *et al.*, 2005; Nord and Haupt, 2005; Kuwata *et al.*, 2007; Kondo *et al.*, 2009) we investigated the performance of this particular TD. This study highlights the importance of correcting data prior to analysis, which presumes normalisation of the volatility data for these correction factors.

The other part of this study was an experimental characterisation of aerosol losses inside diffusion dryers. Diffusion dryers are commonly used to remove some of the gas phase components such as water vapour or volatile organic compounds (VOCs). In the first case they are filled with silica gel, while the second case typically features the use of activated charcoal. They can influence sampling in two ways. First, particle losses will most likely occur due to diffusion and second, vapour pressure of semi-volatiles might influence the losses as this can lead to changed particle composition as well as size. As diffusion dryers are most commonly used to condition aerosols, it is also very important to investigate the losses inside them.

To determine the relationship between flow rate, particle size and proportion of particles lost inside each of the TSI 3065 thermodenuder and Topas DDU 570/L diffusion dryer, a logistic regression model is fitted. The model is a low rank thin plate, a semi-parametric smoother which is able to flexibly fit non-linear effects (Ruppert *et al.*, 2003). Rather than fitting a polynomial, it is suspected that the losses in a thermodenuder and diffusion dryer will decrease from a maximum loss for smaller diameters and eventually transition to a region where the losses are independent of particle diameter. This behaviour can be modelled with a logistic regression with a low rank thin plate smoother. For each device, the following model is used:

$$\log\left(\frac{\mu_i}{1-\mu_i}\right) = \beta_0 + \beta_1 d_i + \gamma |\kappa - d_i| \quad (1)$$

where μ_i is the predicted loss corresponding to mobility diameter d_i and κ is the knot for the thin plate smoother, representing a change point between the two linear models. Further details of this regression method can be found in the supplementary material.

EXPERIMENTAL

A TSI Low-Flow Thermodenuder Model 3065 (TSI-TD)

We used a commercially available low-flow thermodenuder (model 3065, TSI Inc., Shoreview, MN, USA). Most of the aerosol-conducting pathway is made of glass. The desorber section of the instrument uses a 6.35 mm ($1/4''$) in diameter and 120 mm long convoluted stainless steel tube welded onto a 100 mm long glass “bottleneck” that enlarges to form a shoulder piece housing the stainless-steel grid pipe required to keep the charcoal-pellets from collapsing into the aerosol pathway. The steel-glass interface has a slightly

thicker diameter than the steel or the glass section. It was found to be 13 mm in diameter, whereas the glass extension holding the steel grid pipe at the very end of the desorber section measured already 20 mm. These variations in diameter are important in order to understand the temperature profiles outlined further below. Heating of the desorber section is achieved indirectly by using a heater tape that is wrapped around both the stainless steel pipe and the glassware attached to it. The thermocouple used to operate the heater control loop of the instrument is inserted between the aerosol-conducting tubing and the heater tape.

The adsorber section of this TD has an outer diameter of about 100 mm and covers a length of approximately 700 mm. The diameter of the mesh tube through which the aerosol flows through is $1/2''$. It is capable of holding 6 L of activated charcoal pellets. According to the specifications, the instrument should be operated at flow rates between 0.2–2 L/min, with optimal flow at 0.5 to 1 L/min at a desorptive temperature range covering ambient temperature all the way up to 400°C.

Topas DDU 570/H Diffusion Dryer

The Topas 570/H (Topas, Dresden, Germany) diffusion dryer (70 × 475 mm) consists of an acrylic tube with caps on both ends and tube connectors (8 mm). The aerosol stream passes through three screen meshed pipes (10.35 mm inner diameter, 12.51 mm outer diameter) which are surrounded with activated charcoal. The length of the meshed pipe is 421 mm. Although the length of the diffusion dryer is shorter than the adsorber section of the TSI TD, the residence time within the diffusion dryer is similar to the residence time in the adsorber section of the TSI TD due to the flow being split into 3 screen meshed pipes. That is, residence time inside diffusion dryer with 3 meshed pipes is the same as if the flow was passed through the pipe of a same diameter but three times longer. The length of that tube would be approximately the same as the length of the tube inside TD.

Experimental Description

Losses inside the thermodenuder were measured at three different flow rates (1, 2, 4 L/min) and at two temperatures (room temperature, 150°C and 300°C). The performance of the thermodenuder was assessed using two types of particles - NaCl and lubricating oil particles. NaCl was chosen due to its non-volatility under all experimental temperatures and its ease of generation. The lubricating oil particles were chosen as they mimic the volatile component of diesel exhaust (Sakurai *et al.*, 2003b). Due to their small size (< 30 nm), it is expected that the nucleation mode particles will exhibit large losses.

A nebuliser (BGI Single Jet Collision Nebuliser model CN241) was used to generate particles from a solution of NaCl (99.0%, Sigma- Aldrich) and lubricating oil diluted in ultra-pure water and analytical grade ethanol, respectively. The pressure of the nebulizer was set at 1.5 bar. The NaCl particles were dried by passing them through the diffusion dryer, which was filled with silica gel. Lubricating oil particles were dried by passing the aerosol stream through the

diffusion dryer filled with activated charcoal. The experiments were performed for the particle size range 30–300 nm. To cover the wide range of particles different NaCl solutions concentrations were used. The following ten sizes were pre-selected for NaCl to characterise the losses over the wider size range: 20, 30, 45, 65, 90, 120, 155, 191, 237, 274 nm, and the following four sizes were pre-selected for the lubricating oil particles: 30, 90, 150, 250 nm.

Particle size was pre-selected using Electrostatic Classifier (TSI 3071A). As all the diameters were measured with a scanning mobility particle sizer (SMPS), they represent mobility diameters. A monodisperse aerosol stream was generated, passed through the thermodenuder and the size distribution was measured upstream and downstream from the thermodenuder, a similar setup to the one used by (Miljevic *et al.*, 2009) but with the impingers replaced by the diffusion dryer. Schematic representation of the experimental configuration used in this study is shown in Fig. 1. To ensure losses within the tubing were comparable, the tubes leading to each of the two SMPSs were identical in length.

A correction factor was introduced to account for the small difference in the recorded measurements of the two SMPSs. For this purpose the TD was replaced with conductive tubing and experiment was repeated for 5 sizes (30, 65, 120, 191, 274 nm). A small, but noticeable difference in particle number concentrations was observed and further used to calculate the correction factor.

The second set of experiments was performed to assess the losses inside a commercial diffusion dryer, the Topas DDU 570/H filled with activated charcoal. For this purpose we used commercially available Topas DDU 570/H filled with activated charcoal. The experimental setup and NaCl particle generation were the same as for the thermodenuder experiments. Maximum recommended flow through the diffusion dryer is 4 litres per minute, corresponding to a residence time of 1.6 s. The residence times in our experiments were 6.4 s (1 L/min), 3.2 s (2 L/min) and 1.6 s (4 L/min).

Temperature Profiles

The temperature gradient was recorded by using a 0.5 m long and 1 mm thick thermocouple (TC) attached to a Fluke 80TK TC module and Fluke 75 digital multimeter. The TC was kept centered in the aerosol conducting pathway by housing it within a small metal cage. For a given temperature, the TC was gradually inserted into the desorber stage (in intervals of 10 mm) past the desorber section and further, deep into the proximal section of the adsorber (altogether approx. 400 mm). Temperature profiles were recorded for flow rates ranging from 0.3 to 3 L/min for temperatures in the range of 150 to 400°C, incremented in steps of 50°C. Air

flow was generated using a venturi suction system; the flow rate was measured before and after each temperature scan with a Oibrator bubble flow meter (Sensidyne, Gillibrator, Standard Flow Cell). All temperature measurements were performed with an empty adsorber stage (i.e., no charcoal) to avoid unnecessary contamination.

RESULTS AND DISCUSSION

Temperature Profile

During testing it was found that the thermodenuder showed optimal results only within a very narrow flow window of 1 L/min. The combined effect of the glass-metal interface, the various thicknesses of the heater section itself, and the loosely packed heater tape explains why the temperature profiles in the lower and higher flow ranges revealed different profiles (Fig. 2). Increasing the flow to 1.5 L/min resulted in an M-shaped temperature profile; this pattern became even more pronounced at flow rates of 2 L/min and became extremely distorted at flow rates of 3 L/min (corresponding data were not shown in Fig. 2). Residence times at 2 L/min were reduced to 200 ms and 130 ms at 3 L/min, pushing the heated air bolus far below the threshold temperature value even when the instrument was operated at maximum desorber temperature.

The temperature profiles reveal that the air cooled rapidly before it reached the desorber stage. At a flow-rate of 0.3 L/min, with a residence time of about 1.3 s and a set point of 400°C the maximum temperature in the heating section was over 450°C. By the time the air had reached the desorber section it was cooled down to below 250°C. By increasing the flow to at least 1.5 L/min (with a residence time of 760 ms), the 400°C hot bolus enters the adsorber stage with a temperature of 250°C and a much more uneven temperature profile (see Fig. 2).

Losses inside Thermodenuder

Particle losses inside the thermodenuder result from the combination of three processes: sedimentation, diffusion and thermophoresis. As mentioned, sedimentation will not influence the particle number losses of small particles used in the experiments.

Fig. 3 presents number losses observed in the TSI-TD at room temperature. The effect of flow rate was found to be negligible in exploratory analysis and it was removed from the regression model. At room temperature measured losses are due to diffusion effects that increase as particle size decreases. As expected, the observed losses for NaCl particles are the greatest in the size range below 50 nm. The change point between the two linear models occurred

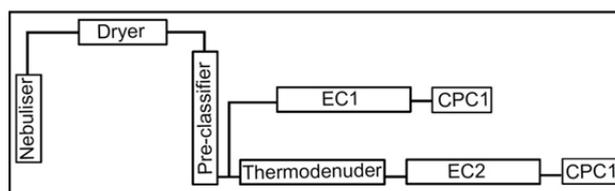


Fig. 1. Schematic representation of the experimental configuration used in this study.

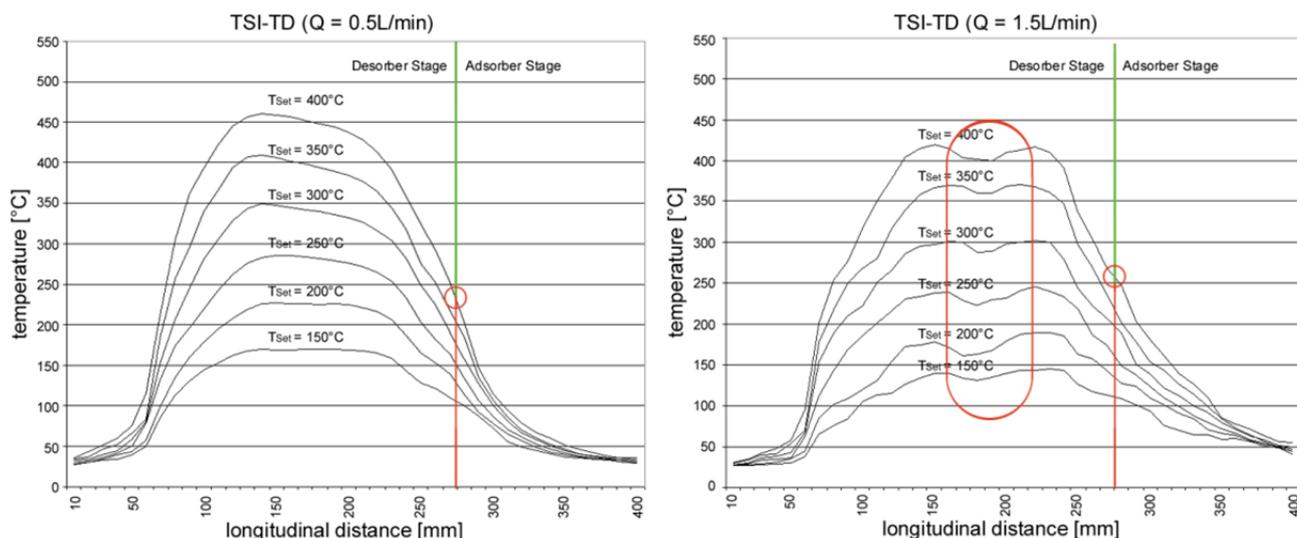


Fig. 2. Temperature profile of the TSI-TD at 0.5 and 1.5 L/min. At a flow-rate of 0.5 L/min (left) the heated bolus of air is not pushed fast enough to the adsorber stage and as a result cools off still within the desorber tube, while a flow rate exceeding 1 L/min (right) results in very distorted temperature profiles.

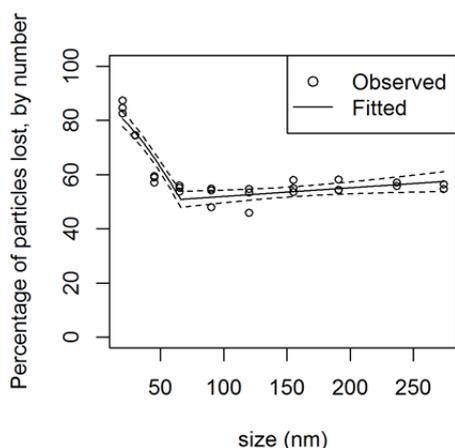


Fig. 3. Open circles (\circ) indicate measured the percentage of NaCl particles lost inside the TSI-TD, by number at room temperature and at three different flow rates (1 L/min, 2 L/min, 4 L/min). The full line is the fitted losses in TSI 3065 based on the logistic regression model, with the dashed line representing the 95% confidence intervals.

at 66 nm. The particle losses are largest for the small particle sizes and the predicted values from the model are in a good agreement with the experimental data ($R^2 = 0.874$). Also, small fluctuations in the case of larger sizes may be attributed to the experimental error.

Particle number losses for NaCl and lubricating oil at 300°C and at three different flow rates are shown in Fig. 4. As mentioned before, diffusive losses change for different particle sizes, while thermophoretic losses are not size dependent for particles in the investigated size-range (Burtscher *et al.*, 2001). Thermophoresis will act to force particles towards the tube centre in the desorbing part and then towards the tube walls as the particle stream enters the adsorbing section. In the case of perfect laminar flow, the

overall effect would be zero.

The number losses curve for NaCl (Fig 4.) shows that at elevated temperature (300°C) particle losses are similar to those at room temperature.

In the case of lubricating oil, however, particle losses increase when the temperature was increased to 300°C. This trend is more obvious at lower flow rates, when particles experience longer residence time inside the TD. The evaporation of semi-volatile components during these long residence times leads to a reduced particle size, resulting in larger diffusional losses. The combination of evaporation, diffusion and thermophoretic effects leads to a removal of 99% of particles smaller than 50 nm.

To illustrate the evaporation process that is occurring when lubricating oil particles are exposed to elevated temperature, the sizes of pre-selected particles before and after the thermodenuder were measured (Fig. 5). Lubricating oil particles evaporate and their diameter decreases significantly. This effect is the most pronounced for the long residence times at the lowest flow rate (1 L/min). This reduction in size leads to increased diffusional losses and explains increased particle losses below 50 nm observed in Fig. 2. No change in particle diameter was observed for NaCl particles as they are nonvolatile.

It is also of note that there are no changes in the particle size for lubricating oil particles at room temperature. Although the air passes through the adsorber section, resulting in absorption of the vapour phase of semivolatile components, the residence time is not sufficiently long for any evaporation from the particle phase to occur.

In order to correct for the losses we have fitted the loss function according to Eq. (1). The loss function for this type of thermodenuder for all flow rates can be expressed as:

$$\log\left(\frac{\mu}{1-\mu}\right) = 0.992 - 0.014d + 0.016|d - 66| \quad (2)$$

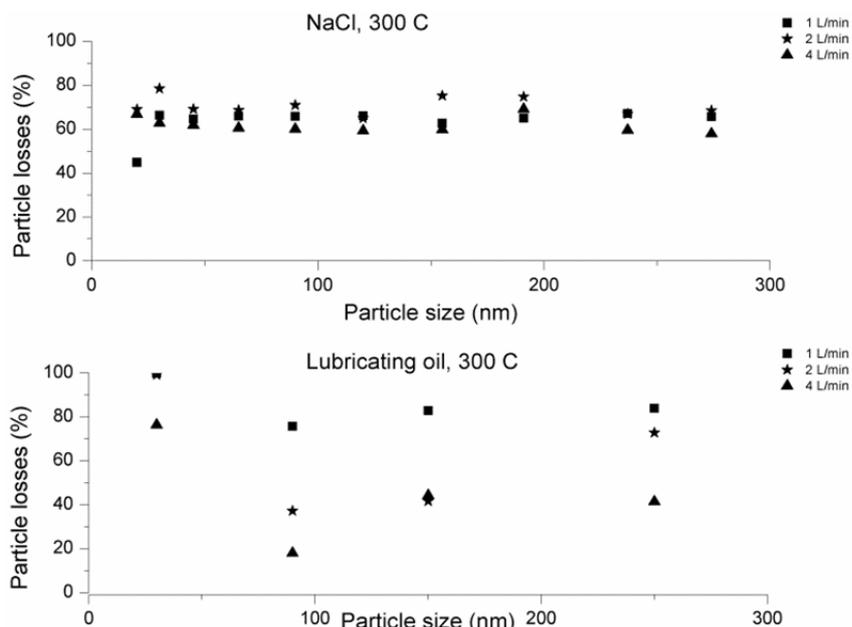


Fig. 4. Particle number losses inside the TSI-TD as a function of size for NaCl and lubricating oil particles at 300°C and three selected flow rates (1 L/min, 2 L/min, 4 L/min).

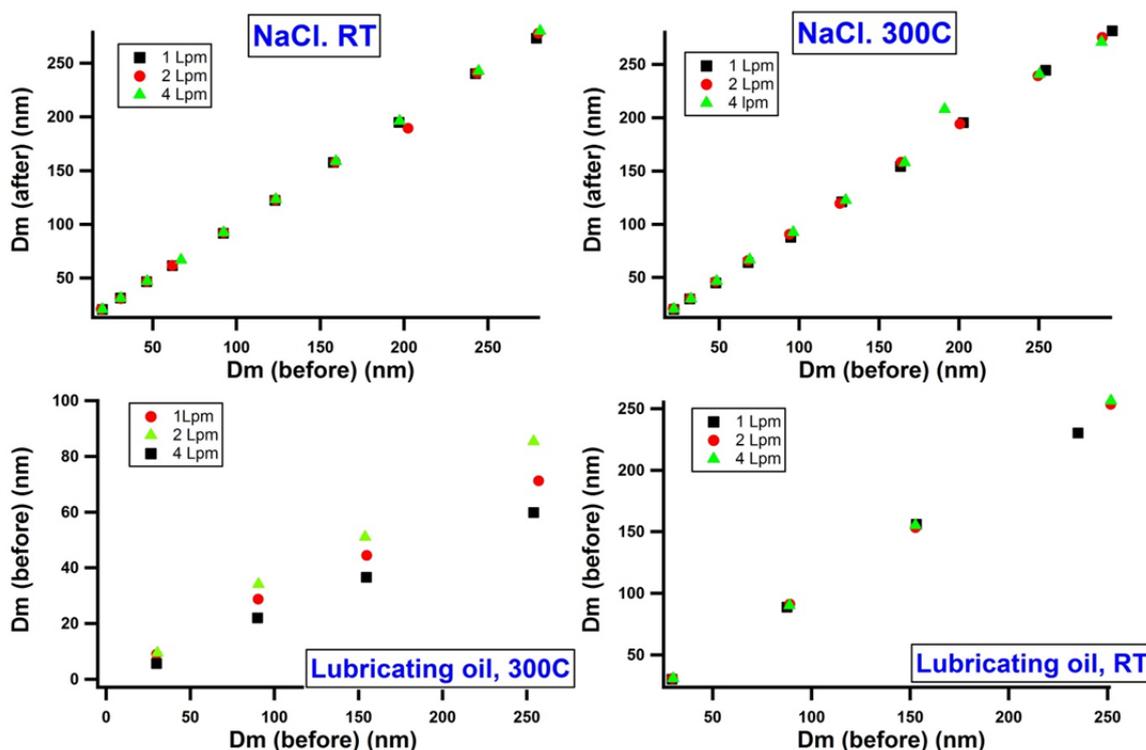


Fig. 5. Measured size of pre-selected NaCl and lubricating oil particles before and after thermodenuder at room temperature and at 300°C. The flow rates of aerosol stream were 1 L/min, 2 L/min and 4 L/min.

where is the loss function and d is the mobility diameter of the particle expressed in nanometres. The fitted function together with the 95% confidence interval is shown on Fig. 2.

Losses inside Diffusion Dryer

In this section, losses were investigated for NaCl

particles inside diffusion dryer at room temperature with activated charcoal. As previously mentioned, the observed losses may be assigned to a process of diffusion. Fig. 6 illustrates particle number losses that were observed at three different flow rates.

As with TD particle losses for NaCl at room temperature,

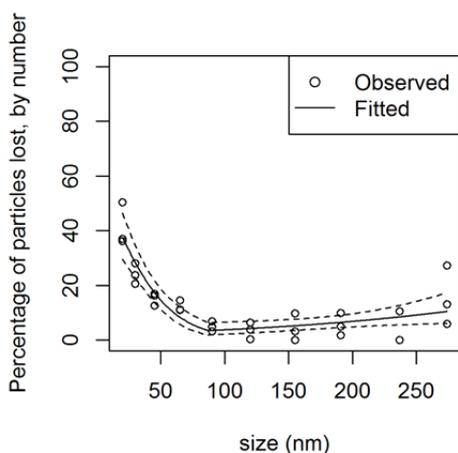


Fig. 6. Open circles (\circ) indicate measured percentage of NaCl particle lost, by number in Topas DDU 570/L diffusion dryer for 1, 2 and 4 L/min, at room temperature. The full line is the fitted losses based on the logistic regression model, with the dashed line representing the 95% confidence intervals.

the biggest losses (15–50%) are for small particles with diameters smaller than 50 nm. The change point occurs at 93nm. The main losses in the TD for small particles are in the adsorber section, which is similar in design to the dryer, i.e., mesh surrounded by charcoal. Number losses for particles bigger than 65 nm are considerably smaller and they are much lower (~10%) for particles bigger than 0.1 μm . Model fit for the thin plate smoother shows good agreement with the data ($R^2 = 0.712$). To enable the correction we have used the same mathematical model as for the TD (Eq. (1)) and applied it for the measurements conducted for the diffusion dryer. The fitted curve together with the 95% confidence interval is shown in Fig. 6. The loss function for this type of diffusion dryer for all flow rates can be expressed as:

$$\log\left(\frac{\mu}{1-\mu}\right) = -1.828 - 0.017d + 0.023|d - 93| \quad (3)$$

CONCLUSIONS

As indicated by the temperature profiles (Fig. 2), the design of the TSI 3065 thermodenuder's heater stage makes it very difficult to keep the desorber temperature above the required threshold temperature of 250°C. As discussed by Wehner *et al.* (2002) the small dimensions of the desorber stage, which result in short residence times, are the main reason for the incomplete desorptive properties. As the temperature in the desorption stage decreases, only partial removal of the volatile fraction is achieved. An increase in flow (> 1 L/min) slightly compensated for this steep temperature drop, but resulted in an inhomogeneous temperature profile within the heater stage. Such M-shaped temperature fluctuations within the desorber stage are a result of the various thermal properties of steel and glass - especially at the interface. These fluctuations are

undesirable as they result in the formation of particles after the initial temperature peak and there is insufficient time for thermal dissolution when exposed to the second thermal peak (Burtscher *et al.*, 2001).

The investigated thermodenuder has relatively high losses for small particles. The results presented indicate that these losses are higher for smaller particles and higher temperatures, which is consistent with a common pattern that is reported in thermodenuder characterisations.

Diffusion dryers are also commonly used to precondition the inlet air of instruments, either to remove the moisture (dry the air and particles) or to remove the gas phase semivolatile organic species (Venkatachari and Hopke, 2008). If significant portions of the aerosol particles are in the size range below 50 nm a correction for the losses within the diffusion dryer is necessary as the losses can be as large as 50% at this size.

In the case of lubricating oil (a surrogate for semivolatile aerosols observed in diesel exhaust) a significant reduction in the vapour pressure, due to absorption in the charcoal filled diffusion dryer, will not lead to the change in the composition of particles and evaporation of lower volatility compounds over residence times of several seconds exhibited in the dryers.

SUPPLEMENTARY MATERIALS

Supplementary data associated with this article can be found in the online version at <http://www.aaqr.org>.

REFERENCES

- An, W.J., Pathak, R.K., Lee, B.H. and Pandis, S.N. (2007). Aerosol Volatility Measurement Using an Improved Thermodenuder: Application to Secondary Organic Aerosol. *J. Aerosol Sci.* 38: 305–314.
- Biswas, S., Ntziachristos, L., Moore, K.F. and Sioutas. (2007). Particle Volatility in the Vicinity of a Freeway with Heavy-Duty Diesel Traffic. *Atmos. Environ.* 41: 3479–3493.
- Burtscher, H., Baltensperger, U., Bukowiecki, N., Cohn, P., Hüglin, C., Mohr, M., Matter, U., Nyeki, S., Schmatloch, V., Streit, N. and Weingartner, E. (2001). Separation of Volatile and Non-Volatile Aerosol Fractions by Thermodesorption: Instrumental Development and Applications. *J. Aerosol Sci.* 32: 427–442.
- Gramacy, R.B. (2007). An R Package for Bayesian Nonstationary, Semiparametric Nonlinear Regression and Design by Treed Gaussian Process Models. *J. Stat. Softw.* 19: 1–46.
- Gramacy, R.B. and Lee, H.K.H. (2008). Bayesian Treed Gaussian Process Models with an Application to Computer Modeling. *J. Am. Stat. Assoc.* 103: 1119–1130.
- Johnson, G.R., Ristovski, Z. and Morawska, L. (2004). Method for Measuring the Hygroscopic Behaviour of Lower Volatility Fractions in an Internally Mixed Aerosol. *J. Aerosol Sci.* 35: 443–455.
- Johnson, G.R., Ristovski, Z., D'Anna, B. and Morawska, L. (2005). Hygroscopic Behavior of Partially Volatilized

- Coastal Marine Aerosols Using the Volatilization and Humidification Tandem Differential Mobility Analyzer Technique. *J. Geophys. Res.* 110: D20203.
- Jonsson, Å.M., Hallquist, M. and Saathoff, H. (2007). Volatility of Secondary Organic Aerosols from the Ozone Initiated Oxidation of α -Pinene and Limonene. *J. Aerosol Sci.* 38: 843–852.
- Kondo, Y., Sahu, L., Kuwata, M., Miyazaki, Y., Takegawa, N., Moteki, N., Imaru, J., Han, S., Nakayama, T., Kim Oanh, N.T., Hu, M., Kim, Y.J. and Kita, K. (2007). Dependence of CCN Activity of Less Volatile Particles on the Amount of Coating Observed in Tokyo. *J. Geophys. Res.* 112: D11207.
- Kondo, Y., Sahu, L., Kuwata, M., Miyazaki, Y., Takegawa, N., Moteki, N., Imaru, J., Han, S., Nakayama, T., Kim Oanh, N.T., Hu, M., Kim, Y.J. and Kita, K. (2009). Stabilization of the Mass Absorption Cross Section of Black Carbon for Filter-Based Absorption Photometry by the Use of a Heated Inlet. *Aerosol Sci. Technol.* 43: 741–756.
- Kulmala, M., Pirjola, L. and Mäkelä, J.M. (2000). Stable Sulphate Clusters as a Source of New Atmospheric Particles. *Nature* 404: 66–69.
- Mauderly, J.L. and Chow, J.C. (2008). Health Effects of Organic Aerosols. *Inhalation Toxicol.* 20: 257–288.
- Meyer, N.K. and Ristovski, Z. (2007). Ternary Nucleation as a Mechanism for the Production of Diesel Nanoparticles: Experimental Analysis of the Volatile and Hygroscopic Properties of Diesel Exhaust Using the Volatilization and Humidification Tandem Differential Mobility Analyzer. *Environ. Sci. Technol.* 41: 7309–7314.
- Miljevic, B., Modini, R.L., Bottle, S. and Ristovski, Z. (2009). On the Efficiency of Impingers with Fritted Nozzle Tip for Collection of Ultrafine Particles. *Atmos. Environ.* 43: 1372–1376.
- Nord, K. and Haupt, D. (2005). Reducing the Emission of Particles from a Diesel Engine by Adding an Oxygenate to the Fuel. *Environ. Sci. Technol.* 39: 6260–6265.
- Robinson, A.L., Donahue, N.M., Shrivastava, M.K., Weitkamp, E.A., Sage, A.M., Grieshop, A.P., Lane, T.E., Pierce, J.R. and Pandis, S.N. (2007). Rethinking Organic Aerosols: Semivolatile Emissions and Photochemical Aging. (REPORTS). *Science* 315: 1259.
- Ruppert, D., Wand, M.P. and Carroll, R.J. (2003). *Semiparametric Regression*, Cambridge University Press.
- Sakurai, H., Park, K., McMurry, P.H., Zarling, D.D., Kittelson, D.B. and Ziemann, P.J. (2003a). Size-Dependent Mixing Characteristics of Volatile and Nonvolatile Components in Diesel Exhaust Aerosols. *Environ. Sci. Technol.* 37: 5487–5495.
- Sakurai, H., Tobias, H.J., Park, K., Zarling, D., Docherty, K.S., Kittelson, D.B., McMurry, P.H. and Ziemann, P.J. (2003b). On-Line Measurements of Diesel Nanoparticle Composition and Volatility. *Atmos. Environ.* 37: 1199–1210.
- Venkatachari, P. and Hopke, P. (2008). Development and Laboratory Testing of an Automated Monitor for the Measurement of Atmospheric Particle-Bound Reactive Oxygen Species (ROS). *Aerosol Sci. Technol.* 42: 629–635.
- Wehner, B., Philippin, S., Wiedensohler, A. (2002). Design and Calibration of a Thermodenuder with an Improved Heating Unit to Measure the Size-Dependent Volatile Fraction of Aerosol Particles. *J. Aerosol Sci.* 33: 1087–1093.

Received for review, December 10, 2013

Revised, March 24, 2014

Accepted, June 5, 2014

Supplementary Material

Ruppert *et al.* (2003) define a univariate low rank thin plate spline as the sum of a polynomial fixed effect and polynomial random effects. The partial effect of a low rank thin plate spline with J random effects of order p as

$$\beta_1 x_i + \dots + \beta_m x_i^m + \sum_{j=1}^J u_j \gamma_j |x_i - \kappa_j|^p$$

where κ are the knots (control points) of the spline and are usually placed at the $J + 2$ quantiles of x . The order of the random effects, p , is chosen to be low (typically 1 to 3), as is the order of the fixed effect (typically chosen to be linear). The low rank thin plate spline is an example of semi-parametric regression and provides a balance between flexible modelling and interpretable parameters. The parameters to be estimated in the regression model are β and γ parameters.

The regression model in this paper uses the logistic link function, $\log\left(\frac{\mu}{1-\mu}\right)$, as the response variable is the proportion of particles lost and can only take values between 0 and 1. To determine the location of the single knot in the regression model as a change point, a treed Gaussian process with a piecewise linear mean function is fit to the data (Gramacy, 2007, Gramacy and Lee, 2008). Because the regression uses the logistic link, the treed GP is inappropriate for the full modelling as the 95 CIs should be heavily asymmetric at values near 0 and 1. Fitting of this logistic GLM is performed in R with the **glm** function. Confidence intervals for the fitted low rank thin plate spline are obtained from **glm** and are appropriately asymmetric because the logistic function is not a linear transformation.

Losses were measured at the following sizes (in nanometres): 20, 30, 45, 65, 90, 120, 155, 191, 237 and 274. The change points were 66 for the thermodenuder and 93 for the diffusion dryer.

Flow rate had been included in the regression model but was found to have a negligible effect in each case (the coefficient for a linear term was zero with p values of 0.8792 for the thermodenuder and 0.9686 for the diffusion dryer) so flow rate was ignored in the regression modelling.