On the performance of a calibrated nanoparticle generator

Ulrika Backman¹, Jussi Lyyränen¹, Unto Tapper¹, Ari Auvinen¹ and Jorma Jokiniemi¹,²

¹VTT Technical Research Centre of Finland, Fine Particles, P.O. Box 1000, FI-02044 VTT, Finland,
²University of Kuopio, Department of Environmental Science, Fine Particle and Aerosol Technology Laboratory, P.O. Box 1627, FI-70211 Kuopio, Finland.

E-mail: Ulrika.Backman@vtt.fi

Abstract. There is a need for nanoparticle generators with well characterised properties in many fields. For instance the calibration of measurement instruments can be done in place and the downtime for the instrument hence decreased. Also in nanoparticle toxicity experiments it is very important to have a well characterised particle source [1]. The aim of this study was to develop a calibrated nanoparticle generator with stable particle production. The number concentration should be regulated over many orders of magnitude and the particle size should also be adjustable. In this paper the design of the nanoparticle generator and the properties of the produced nanoparticles at one furnace temperature are presented.

The nanoparticle generator designed and developed is based on the formation of titania nanoparticles via thermal decomposition of titanium tetraisopropoxide (TTIP) at atmospheric pressure. This process was chosen as it is a well known and studied process [2-5]. The effect of the residence time and reaction temperature on the produced titania nanoparticles has among other parameters been studied. Also the decomposition reaction of TTIP has been studied and it has been reported that in addition to TiO₂ particles also the following gaseous components form: acetone (C₃H₆O), isopropanol (C₃H₈O), propene (C₃H₆) and water (H₂O) [6, 7].

Our setup, presented in figure 1, consists of a bubbler and a laminar flow reactor. The bubbler with the precursor, titanium tetraisopropoxide (TTIP, CAS# 546-68-9, 97%, Sigma-Aldrich Co.), is immersed in a water bath in order to keep it at a constant temperature. The temperature in these experiments was kept at 30°C. The precursor is vaporised by bubbling nitrogen gas through the liquid TTIP at a flow rate (MFC1 in Figure 1 and Table 1) between 1 l/min and 5 l/min. This gas flow was heated prior to the bubbler using heating tape to the same temperature as the water bath i.e. in this case 30°C.

The tubing from the bubbler to the furnace was heated with heating tape to 155°C in order to prevent the precursor from condensing before reaching the furnace. An additional nitrogen carrier gas flow (MFC2 in Figure 1 and Table 1) is fed from the bottom of the furnace at a flow rate between 2 l/min and 10 l/min, always being twice as much as the bubbler flow (MFC1). This flow (MFC2) is pre-heated to 155°C before entering the furnace.

The furnace consists of two heating zones, the preheating zone was set to 155°C and the reaction zone was set to 600°C, 700°C or 800°C. The preheating zone is 17 cm long and the reaction zone 63 cm long. The inner diameter of the quartz glass furnace tube is 18 mm. After the furnace the
particle-laden gas is diluted with air (MFC3 in Figure 1 and Table 1) using a coaxial glass diluter. Before the sampling further dilution is done using a porous tube diluter (MFC4 in Figure 1 and Table 1) and two ejector diluters. The dilution gas is air in all three diluters. The flows to the ejector diluters were kept constant in all experiments at 50 Nl/min and 68 Nl/min, respectively. The total dilution ratio as compared to the bubbler flow is kept rather constant, between 2200 and 2600, in all experiments. All the flow rates are controlled with mass flow controllers (Brooks Instruments BV.), except the second ejector diluter flow which is controlled using a critical orifice. The different flow rates and the experimental parameters used in the experiments are presented in Table 1. In this paper only the results from experiments done at a furnace temperature of 700°C are presented.

The particle number concentration of the produced titania nanoparticles was measured with a Condensation Particle Counter (CPC, TSI Inc. model 3022). With this instrument particles above 7 nm in size at maximum concentrations of $10^7$ particles/cm$^3$ can be measured. The instrument was operated at a flow rate of 0.3 l/min. The particle number size distribution was measured with a Scanning Mobility Particle Sizer (SMPS) consisting of a Differential Mobility Analyser (DMA, TSI Inc. model 3081) and a Condensation Particle Counter (CPC, TSI Inc. model 3775). With this setup particles between 6 nm and 225 nm can be detected, when the CPC was operated at a high flow rate, i.e. 1.5 l/min and a sheath flow of 15 l/min is used in the DMA. The system was controlled with the Aerosol Instrument Manager (TSI) and in the data processing both multiple charge correction as well as diffusion correction was taken into account.

The composition of the gas exiting the furnace was monitored using a Fourier Transform Infrared (FTIR) Spectrometer (Gasmet Dx-4000). Monitoring the gas phase compounds using FTIR gives us an opportunity to see if the reaction temperature is high enough and/or the residence time is long enough for the decomposition reaction to be complete. This is important because if unreacted TTIP exits the furnace, large, several hundred nanometer size particles are formed when the vapour phase TTIP condenses.

Figure 1. Schematic figure of the experimental setup used in this study.

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Table 1. The parameters of the experiments carried out for this study. For more detail on the flow rates MFCi, see Figure 1.

| Experiment # | Furnace temperature [°C] | Bubbler flow MFC1 [l/min] | Flow MFC2 [l/min] | Dilution flow MFC3 [l/min] | Porous tube diluter MFC4 [l/min] |
|--------------|-------------------------|---------------------------|-----------------|---------------------------|---------------------------------|
| 1            | 700                     | 1                         | 2               | 9.98                      | 5.988                           |
| 2            | 700                     | 2                         | 4               | 19.96                     | 11.976                          |
| 3            | 700                     | 3                         | 6               | 29.94                     | 17.964                          |
| 4            | 700                     | 4                         | 8               | 39.92                     | 23.952                          |
| 5            | 700                     | 5                         | 10              | 49.9                      | 29.94                           |

The particle number concentration of two consecutive experiments is presented in Figure 2 for the five different flow rates at a furnace temperature of 700°C. The results are corrected for the dilution. We can see that the number concentration stays stable during one condition and from day to day. We can also see from the figure that the total particle number concentration first increases when increasing the flow rate through the bubbler, up to a flow rate of 3 l/min. After that the particle number concentration decreases when increasing the flow rate. This decrease in the particle number concentration indicates that the decomposition reaction of TTIP is not complete.

The particle number size distribution for the five different bubbler flow rates at a furnace temperature of 700°C is presented in Figure 3. From the figure we can see that smaller particles are produced when increasing the flow rate and thus decreasing the residence time, allowing less time for agglomeration and reaction. Also here the decrease in total number concentration at flow rates higher than 3 l/min is seen.

Figure 2. Total particle number concentration of titania particles produced at 700°C and different bubbler flow rates.

Figure 3. Number particle size distribution of titania particles produced at 700°C and varying bubbler flow rate.
The gas-phase compounds produced during the experiments at a furnace temperature at 700°C are presented in Figure 4. From the figure we can see that increasing the bubbler flow rate from 1 l/min to 2 l/min does not have an effect on the concentration of propene. However, a further increase in the flow rate decreases the propene concentration. This is due to an uncompleted decomposition of the precursor. The increase in isopropanol concentration at higher flow rates also indicates this. The level of acetone is rather low throughout the experiment.

![Figure 4](image-url)  
**Figure 4.** Variation in gas phase composition with different bubbler flow rates at a furnace temperature of 700°C.

**Conclusions**
An aerosol generator producing TiO$_2$ nanoparticles via thermal decomposition of titanium tetraisopropoxide was developed and characterised. The particle number concentration, the particle number size distribution and the gas phase compounds were measured at different bubbler flow rates. It was seen that when increasing the bubbler flow rate the residence time in the furnace decreased so that there was not enough time for the decomposition reaction to be completed. An increase in the flow rate and so decrease in the residence time also resulted in smaller agglomerates as there was less time for agglomeration.

**References**
[1] Oberdörster G, Maynard A, Donaldson K, Castranova V, Fitzpatrick J, Ausman K, Carter J, Karn B, Kreyling W, Lai D, Olin S, Monteiro-Riviere N, Warheit D and Yang H 2005 *Particle and Fibre Toxicology* 2:8
[2] Komiyama H, Kanai T and Inoue H 1984 Chem. Let. 1283
[3] Okuyama K, Kousaka Y, Toghe N, Yamamoto S, Wu J J, Flagan RC and Seinfeld J H 1986 *AIChE Journal* 32(12) 2010
[4] Kirkbir F and Komiyama H 1987 *The Canadian J Chem Eng* 65 759
[5] Backman U, Tapper U and Jokiniemi J K 2004 *Synthetic Metals* 142 169
[6] Fictorie C P, Evans J F and Gladfelter W L 1994 *J. Vac. Sci. Technol. A* 12(4) 1108
[7] Wu Y-M, Bradley D C and Nix M 1993 *Appl. Surf. Sci* 64 21