Final Report

NIOSH Contract No. 254-2005-M-11698

"Penetration of Nanoparticles through Respirator Filter Media"

Prepared by

David Y.H.P ui and Seong Chan Kim

Particle Technology Laboratory

Mechanical Engineering Department

University of Minnesota

111 Church Street, SE

Minneapolis, MN 55455

Submitted to

Dr. Samy Rengasamy

NPPTL, NIOSH

626 Cochrans Mill Road

Pittsburgh, PA 15236

April 2, 2006

University of Minnesota
NIOSH contract # 254-2005-M-11698
Title: "Filtration efficiency of typical respirator filters for nanoscale particles"

<u>Acronyms</u>

ASTM -	American Society for Testing and Materials
COV -	coefficient of variation
CPC -	condensation particle counter
DMA -	differential mobility analyzer
HEPA -	high efficiency particulate air
HVAC -	heating, ventilating, and air conditioning
PTFE -	polytetrafluoroethylene
SMPS -	scanning mobility particle sizer
SEM -	scanning electron microscope
UCPC -	ultrafine condensation particle counter

Abstract

Int his study, nanoparticle penetration was tested for with a wide range of filter media (four fiberglass filter media, four electret filter media and one nanofiber filter media) using silver nanoparticles from 3 nm to 20 nm at face velocities of 5.3, 10 and 15 cm/s. The silver particles were generated by heating a pure silver powder source via an electric furnace with a temperature of 870°C, which is the optimal temperature for generating adequate amounts of silver nanoparticles for the size range specified above. After size classification using a nano-DMA, the particle counts were measured by aU CPC both upstream and downstream of the test filter to determine the nanoparticle penetration for each particular particle size. Particle sampling time continued long enough to detect more than 10^5 counts at the upstream and 10 counts at the downstream sampling point so that 99.99% efficiency can be detected with the high efficiency filter. Each test was repeated more than five times by different operators, at different dates and with different samples from each filter medium in order to reduce any possible error. The results show a very high uniformity with small error bars for all filter media tested in this study. The particle penetration decreases continuously down to 3 nm as expected by the traditional filtration theory,

and together with a companion modeling study by Wang et al. (2006), we found no evidence of nanoparticle thermal rebound down to 3 nm.

Introduction

Nanotechnology, which involves the manipulation of matter at nanometer length scales to produce new materials, structures and devices, has the potential to start the new industrial revolution of today. The potential for new products leading to improvements in our lives is astounding. Nanoparticles often behave much differently than bulk samples of the same materials, resulting in unique electrical, optical, chemical, and biological properties. The special properties of nanoparticles give riset o recent concerns about the potential health hazards posed to workers or users that are exposed to them. Therefore, nanoparticle researchesha ve received considerable attention in many laboratories and industrial fields, especially for studying the health effects of nanoparticles and their control.

Filtration is the simplest and most common method for air cleaning, and aerosol filtration is used in diverse applications, such as respiratory protection, air cleaning of smelter effluent, processing of nuclear and hazardous materials, and clean rooms. However, the process of filtration is complicated, and although the general principles are well known there is still aga p between theory and experiment (Hinds, 1999). In particular, recent modeling and experiments pointed to the potential penetration of nanoparticles through the filters due to thermal rebound. Further, nanoparticle penetration has not been shown clearly due to the difficulties of system set-up and particle measurement. Wang and Kasper (1991) suggested a numerical model for nanoparticle penetration showing that the thermal impact velocity of a particle will exceed the critical sticking velocity in the size range between 1 and 10 nm depending sensitively on elastic and surface adhesion parameters. Ichitsubo et al. (1996) conducted an experimental work of nanoparticle penetration using wire screens, and showed the nanoparticle penetration below two nm in size was higher than the theoretical results due to the thermal rebound. Following this, Alonso et al. (1997) used a tandem DMA technique, and detected no particle bounce effects in the same size range as Ichitsubo et al. However, Balazy et al. (2004) measured the nanoparticle penetration of fibrous filter media and showed the decrease of the filtration efficiency at the particle size of 20 nm due to the thermal rebound. However, as of now, the thermal rebound effect on nanoparticle filtration is not well proven, and it is very important to study the air filtration properties of nanoparticles to determine the filtration requirements of personal protective equipment.

In this study, the nanoparticle penetration test system has been established and the nanoparticle penetration was tested with a wide range of filter media (four fiberglassf ilter media, four electret filter media and one nanofiber filter media) using silver nanoparticles from 3 nm to 20 nm at face velocities of 5.3, 10 and 15 cm/s.

Experiments

Fig. 1 shows as chematic diagram of a nanoparticle filtration test system, and it consists of a nanoparticle generation system, a size classification system and a penetration measurement system. Ane lectric furnace is used to generate silver nanoparticles from a pure silver powder source (99.999%, Johnson Mattney Electronics), and clean compressed air is used as a carrier gas with flow rate of 3.0 lpm. The silver powder source located in the center of a heating tube is vaporized and condensed into silver nanoparticles with a wide size distribution at colder parts. The particle size distribution can be controlled by the furnace temperature as shown in Fig. 2. The average size and the particle number concentration ofs ilver nanoparticles generated by the furnace increases with the temperature because a higher temperature increases the evaporation rates and the enlarged mass of condensable vapor enables the particles to grow to larger sizes by condensation (Scheibel and Porstendorfer, 1983).

The silver nanoparticles are given a Boltzman charge distribution by Po-210 and classified by a differential mobility analyzer (nano-DMA, Model

3085, TSI). Then, the neutralized silver nanoparticles by another Po-210 are introduced to test filter and the number counts upstream and downstream of the filter are measured by an ultrafine CPC (Model 3025A, TSI) for the nanoparticle penetration calculation during a certain sampling time. The particle sampling time continued long enough to detect more than 10^5 counts at the upstream and 10 counts at the downstream sampling point so that 99.99% efficiency can be detected with the high efficiency filter. Each test is repeated more than five times by different operators, at different dates and with different samples from each filter medium in order to reduce any possible error.

Chen et al. (1998) studied nanoparticle transportation in the nano-DMA in order to reduce nanoparticle loss and suggested a new inlet design to reduce the recirculation problem. Here, the slit width is reduced to improve the matching of the flow velocity in the classifying region and to avoid electric field penetration into the upstream side of the entrance slit. As a result, the nano-DMA hast he potential for high resolution in sizing and classifying nanoparticles. Fig. 3 shows the calibration results of nano-DMA measured by SMPS (Model 3080, TSI) and CPC (Model 3022A, TSI). These size distributions were measured next to the nano-DMA for the particle size classification and the results show that nanoparticle size distribution classified by nano-DMA is mono disperse and acceptable for a discrete nanoparticle penetration test.

Table 1 shows the specifications of the four different fiberglass filter papers tested in this study. The filter papers were made by the manufacturer, Hollingsworth and Vose of East Walpole, MA 02032, U.S.A, and were originally donated for use in the establishment of the precision and accuracy statement for the ASTM F1215-89 Standard "Standard Method for Determining the Initial Efficiency of a Flatsheet Filter Media in an Airflow Using Latex Spheres". The filter papers are of very low variability, with coefficients of variation for thickness, mass per area, initial pressure drop and initial DOP penetration of less than 4, 1, 2 and 3 %, respectively (Japuntich, 1991). HE series approach HEPA regime for small particle size and HF series is more common to standard HVAC systems. These filter media have different combinations of supporting fibers to keep filter shape and main fibers to capture particles, and the filtration efficiency is proportional to the amount of the main fibers. Fig. 4 shows the SEM images of H&V fiberglass filter media magnified 500 times. The pore size of HE filter media is much smaller than that of HF filter media, and vice versa for the fiber diameter, and the main fiber ratio of HE filter media is much higher that of HF filter media.

Table 2 shows a list of commercial filter media that were tested in this study. Four different electret filter media (media A, B, C, and D)a re made by 3M Company and Lydall, Inc. and applied on commercial respirators that are widely used in the working field. Media E is a nanosized e-PTFE (expanded polytetrafluoroethylene) membrane filter medium made by W.L. Gore, and is used for ultra high efficiency filtration industrial applications. Fig. 5 shows the SEM images of the commercial filter media tested in this study. The uniformities of the porosity are not asgo od when compared to the H&V fiberglass filter media as shown in the SEM images, but media E can be expected to show high repeatability in test results due to its uniform porosity all over the filter medium.

Each filter sample was placed in a portable filter holder with a filtration area of 17.34 cm^2, and the face velocity through the test filter medium was controlled by a regulated vacuum pump located at the end of the system. The tests were conducted with face velocities of 5.3, 10.0, and 15.0 cm/s. Prior to each test, a particle count measurement at the downstream end of the test filter with applying zero Volts to the nano-DMA was conducted in order to check the leakage of the filter holder. And after switching the sampling point from upstream to downstream, another zero V nano DMA-measurement was conducted to make sure that there is no residual particle inside the sampling tube.

Results and discussion

Nanoparticle penetration efficiencies were conducted for four different fiber glass filter media, four different electret filter media and one nanofiberf ilterm edium using silver nanoparticles. All experimental results are shown in terms of the percent penetration with respect to the electrical mobility diameter that is classified the by nano-DMA. Each data point is an average of at least five replicates with the maximum and minimum values as error bars. Each test was conducted by different operators, at different dates and with different samples from each filter medium in order to reduce any possible error. Fig. 6 shows the nanoparticle penetration of the H&V fiberglass filter media at the face velocity of 5.3 cm/s, which is a standard test velocity for a respirator filterm edium. The furnace setting temperature was 870°C, which can generate an adequate amount of silver nanoparticles for the size range of 3 to 20 nm. The particle sampling time continued long enough to detect more than 10^5c ounts at the upstream and 10 counts at the downstream sampling point so that 99.99% efficiency can be detected with the high efficiency filter. The results show a very high uniformity with small error bars. In the case of the HF 0012, which has the lowest filtration efficiency among the H&V fiber glass filter media, data was obtainable for all particle sizes down to 3 nm, while the particle penetration less than 9 nm for the HE 1073 could not be measured due to its high filtration efficiency. In these cases, particles cannot be measured at the downstream sampling point, even with an extended sampling time of 30 minutes. The results show that particle penetration decreases continuously down to 3 nm as expected by the traditional filtration theory, and there is no significant evidence of the nanoparticle thermal rebound down to 3 nm.

Fig. 7 and 8 show the nanoparticle penetration of the H&V fiberglass filter media at the face velocity of 10 and 15 cm/s, respectively. The higher face velocities show a higher penetration percentage due to a shorter residencet imet hrough the filtration region. Theser esults show the same trend with the case of the 5.3 cm/s face velocity. Fig. 9 shows the nanoparticle penetration of the commercial filter media at the face velocity of 5.3 cm/s. Nanoparticle penetration decreases continuously with decreasing particle size down to 3 nm with no evidence of thermal rebound. These results show larger error bars than those of the H&V fiberglass filter media due to a non-uniformity of the fiber diameter, porosity and fiber charging condition except media E as mentioned previously.

Fig. 10 shows the combination of the nanoparticle penetration done in this study with the submicron particle (from 20 to 200 nm) penetration done by Japuntich et al. (2005) for H&V fiberglass filter media at the face velocity of 5.3 cm/s. They used a TSI 8160 automated filter tester for the particle penetration test with sodium chloride (NaCl) particles generated by an atomizer. As shown in the graph, the results agree well with each other at the particle size of 20 nm, even though different test particles were challenged for each result. This is because the most dominant filtration mechanism for nanoparticles is Brownian diffusion, which is not affected by the particle density.

Conclusion

Int his study, the nanoparticle penetration was tested with a wide range of filter media (four glass fiber filter media, four electret filter media and one nanofiber filter media) using silver nanoparticles from 3 nm to 20 nm at face velocities of 5.3, 10 and 15 cm/s. Nano-DMA calibration and adequate leakage tests show that the test system can produce a repeatable and reliable data. Each test was conducted more than five times by different operators, at different dates and with different samples from each filter medium in order to reduce any possible error. The furnace setting temperature was determined to generate large amounts of silver nanoparticles for the size range of 3 to 20 nm, and the particle sampling time continued long enough to detect more than 10^5 counts at the upstream and 10 counts at the downstream sampling point so that 99.99% efficiency can be detected with the high efficiency filter. The results show a very high repeatability with small error bars for all filter media tested in this study. The particle penetration decreases continuously down to 3 nm as expected by the traditional filtration theory, and there is no significant evidence of the nanoparticle thermal rebound down to 3 nm for nine different filter media and three different face velocities. Further, the result shows a good agreement in the overlapping size range of previous test results challenging submicron particles (from 20 to 200 nm).

References

Alonso, M., Y. Kousaka, T. Hashimoto, and N. Hashimoto, 1997, Penetration of nanometer-sized aerosol particle through wire screen and laminar flow tube, Aerosol Science and Technology, Vol. 27, pp. 471-480.

Balazy, A., A.P odgorsky and L. Gradon, 2004. EAC Proceeding Vol. II, S967-S968.

Chen, D.-R., D.Y.H. Pui, D. Hummes, H. Fissan, F.R. Quant and G.J. Sem, 1998, Design and evaluation of a nanometer aerosol differential mobility analyzer (Nano-DMA). Journal of Aerosol Science, Vol. 29, No. 5/6, pp. 497-509.

Hinds, W. C.,19 99. Aerosol Technology: Properties, Behavior, and Measurement of Airborne Particles. John Wiley & Sons, New York.

Ichitsubo, H., T. Hashimoto, M. Alonso, and Y. Kousaka, 1996, Panetration of ultrafine particles and ion clusters through wire screen, Aerosol Science and Technology, Vol. 24, pp. 119-127.

Japuntich, D.A.,19 91. Particle clogging of fibrous filters, Ph.D. Thesis, Loughborough University of Technology, Loughborough, U.K.

Japuntich, D.A.,L . Franklin, D.Y.H. Pui,T . Kuehn and S.C.K im, 2005, Air filtration testing the TSI 8160 automated filter tester for solid and liquid aerosol of 15 to 400 nm diameter, Second International Symposium on Nanotechnology and Occupational Health, Minnespolia, MN.

Scheibel, H.G. and J. Porstendorfer, 1983. Generation of Monodisperse Ag- and NaCl- Aerosol with Particle Diameter Between 2 and 300 nm. Journal of Aerosol Science, Vol. 14, No. 2, pp. 113-126.

Wang, H.-C., and G. Kasper, 1991, Filtration efficiency of nanometer-size aerosol particles, Journal of Aerosol Science, Vol 22, pp. 31-41.

Tables and Figures

Table 1. Specifications of H&V fiberglass filter media

Filter Parameters		Media			
		HE1073	HE1021	HF0031	HF0012
Thickness (cm)	Ave. %COV	0.053 2.3	0.069 4.3	0.074 2.3	0.074 2.3
Basis Weight (g/m^2)	Ave. %COV	63.9 0.53	80.3 0.67	82.6 0.86	69.2 0.92
Pressure Drop at 5.3 cm/s (mmH2O)	Ave. %COV	8.4 1.48	4.7 1.35	3.5 1.94	1.3 1.47
DOP % Penetration 0.3 μm at 5.3 cm/s	Ave. %COV	12.8 2.2	39 1.7	45.8 0.92	79.9 1.24
Fiber Density (g/m^3)	-	2.4	2.4	2.4	2.4
Solidity	-	0.050	0.049	0.047	0.039
Effective Fiber Diameter (μm)	-	1.9	2.9	3.3	4.9
Effective Pore Diameter (μm)	-	8.8	13.4	16.1	26.2

Table 2. Specifications of the specialized filter media

Name	Type	Manufacturing Method
Media A	Corona Charged Blown Fiber (mid-size fiber)	Melt Blowing Process
Media B	Highly Charged Blown Fiber (mid-size fiber)	Melt Blowing Process
Media C	Split Film Fiber	Film Extrusion Process
Media D	Highly Charged Blown Fiber (fine-size fiber)	Melt Blowing Process
Media E	e-PTFE Membrane Filter	-

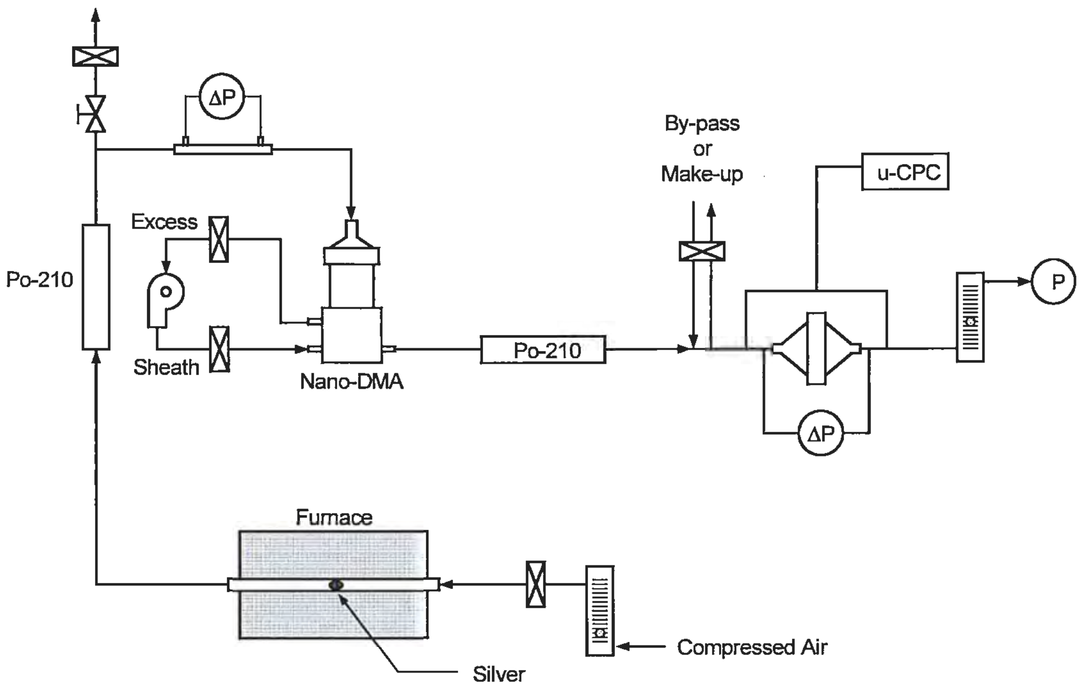


Fig. 1. Schematic diagram of the nanoparticle penetration test

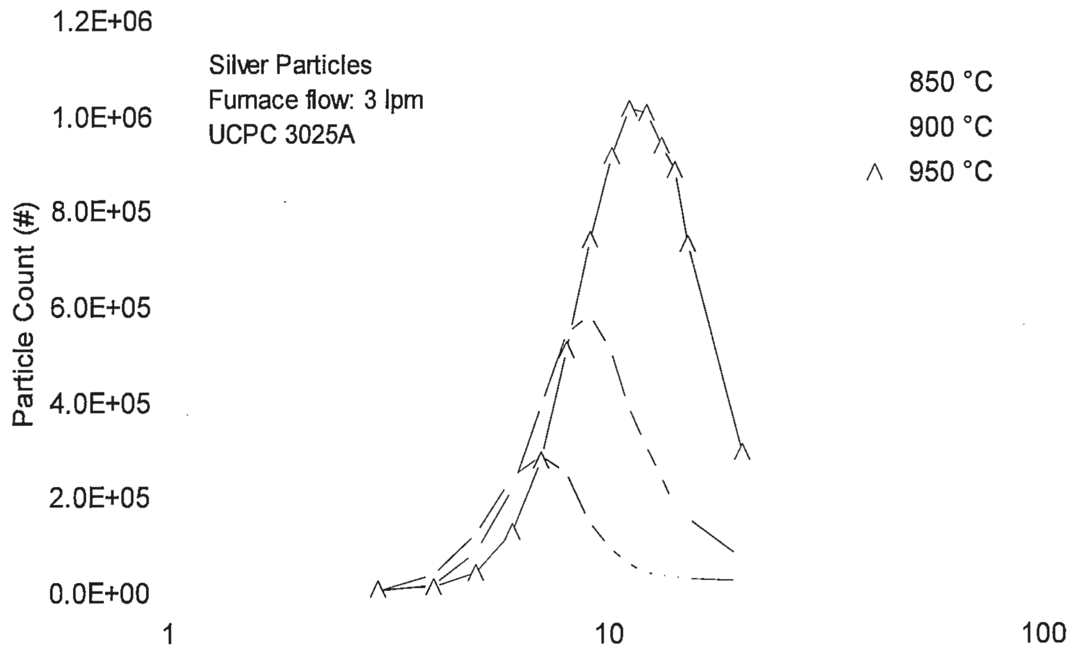


Fig 2. Silver nanoparticle size distribution as a function of temperature

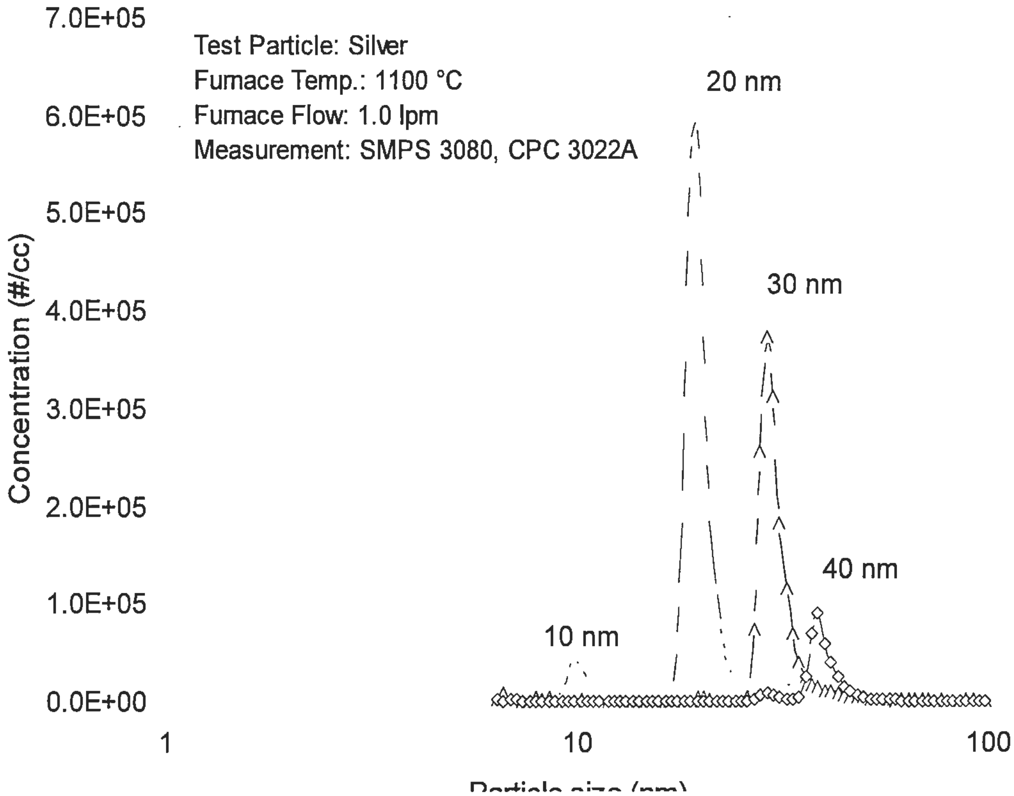
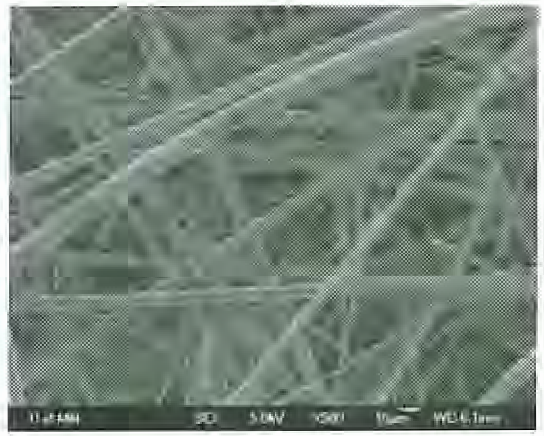
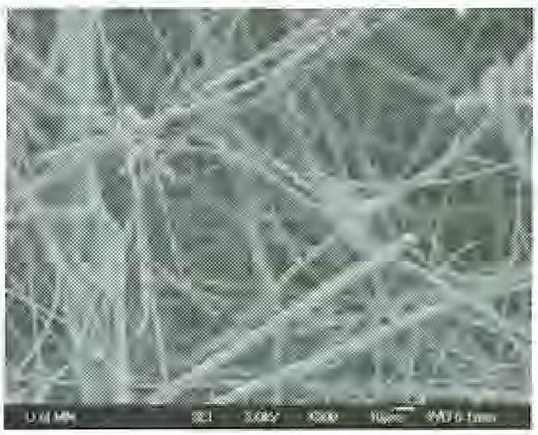


Fig. 3. Nano-DMA calibration

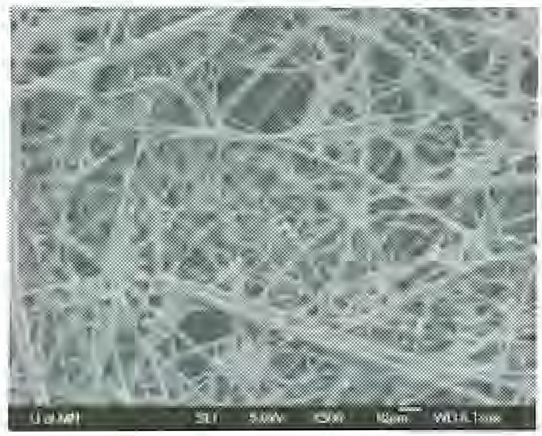
(a) HF0012



(b) HF0031

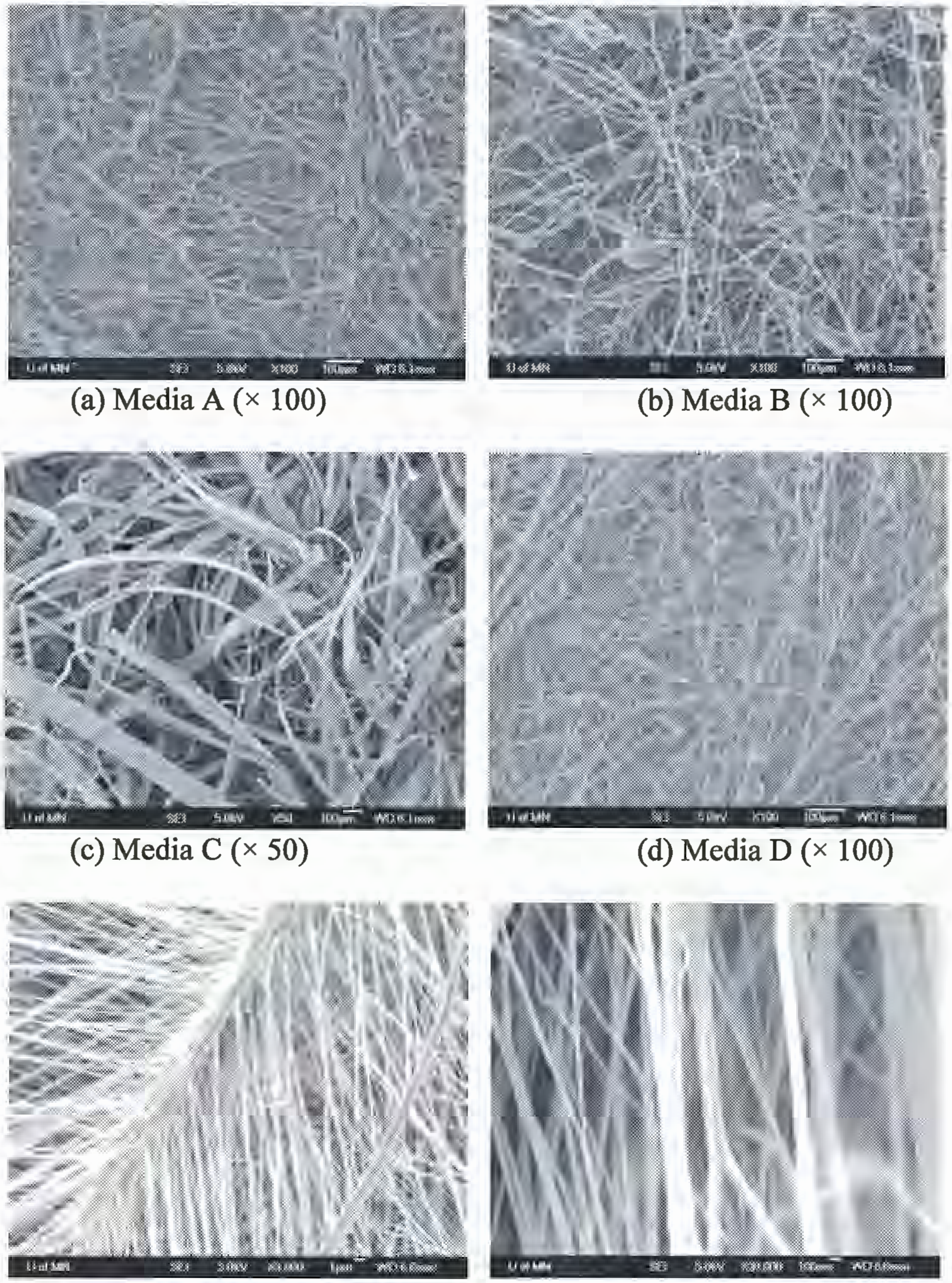


(c) HE1021



(d) HE1073

Fig. 4. SEM images of the H&V filter papers (× 500)



(a) Media A (× 100)

(b) Media B (× 100)

(c) Media C (× 50)

(d) Media D (× 100)

(e) Media E (× 3,000)

(f) Media E (× 30,000)

Fig. 5. SEM image of the specialized filter media

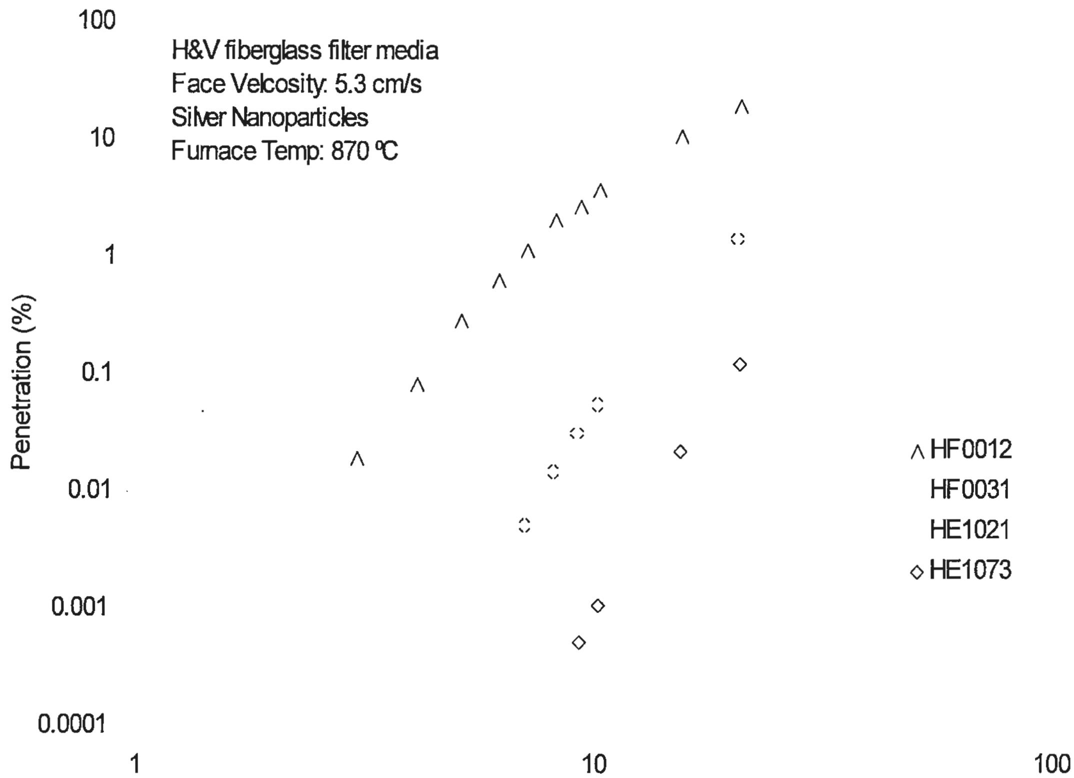


Fig. 6. Nanoparticle penetration of the H&V filters at the face velocity of 5.3 cm/s

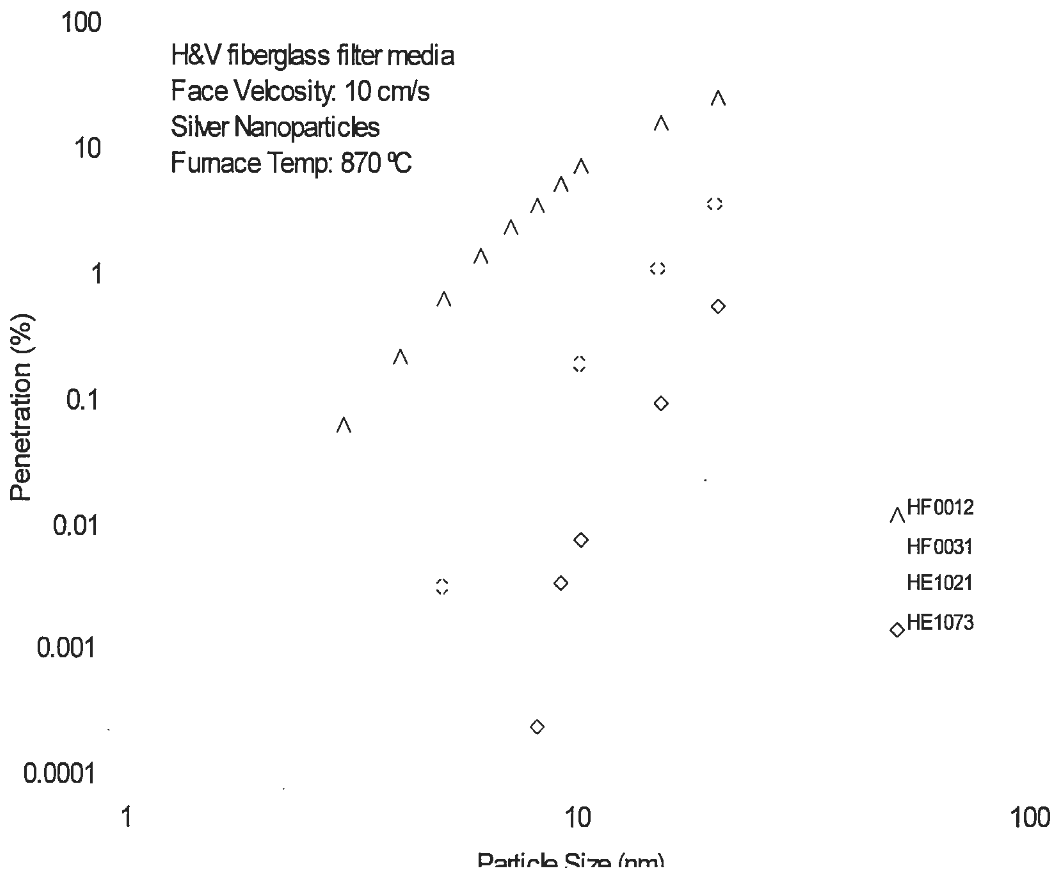


Fig. 7. Nanoparticle penetration of the H&V filters at the face velocity of 10.0 cm/s

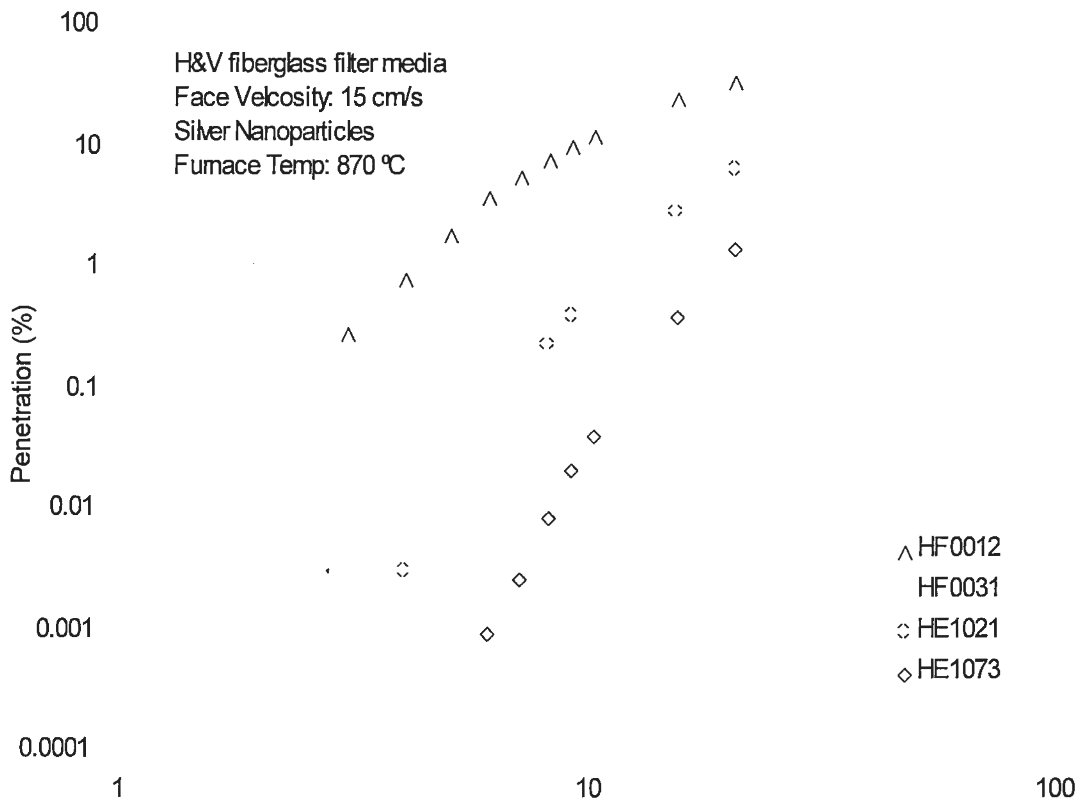


Fig. 8. Nanoparticle penetration of the H&V filters at the face velocity of 15.0 cm/s

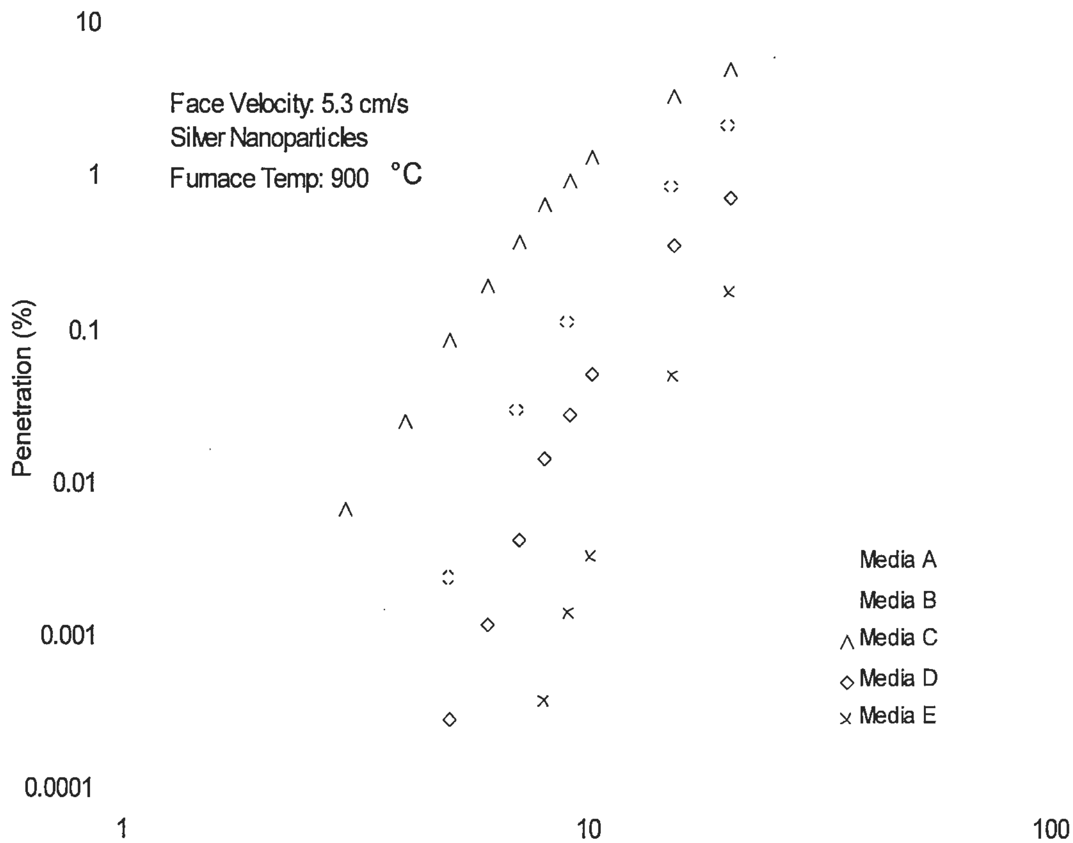


Fig. 9. Nanoparticle penetration of the specialized filter media

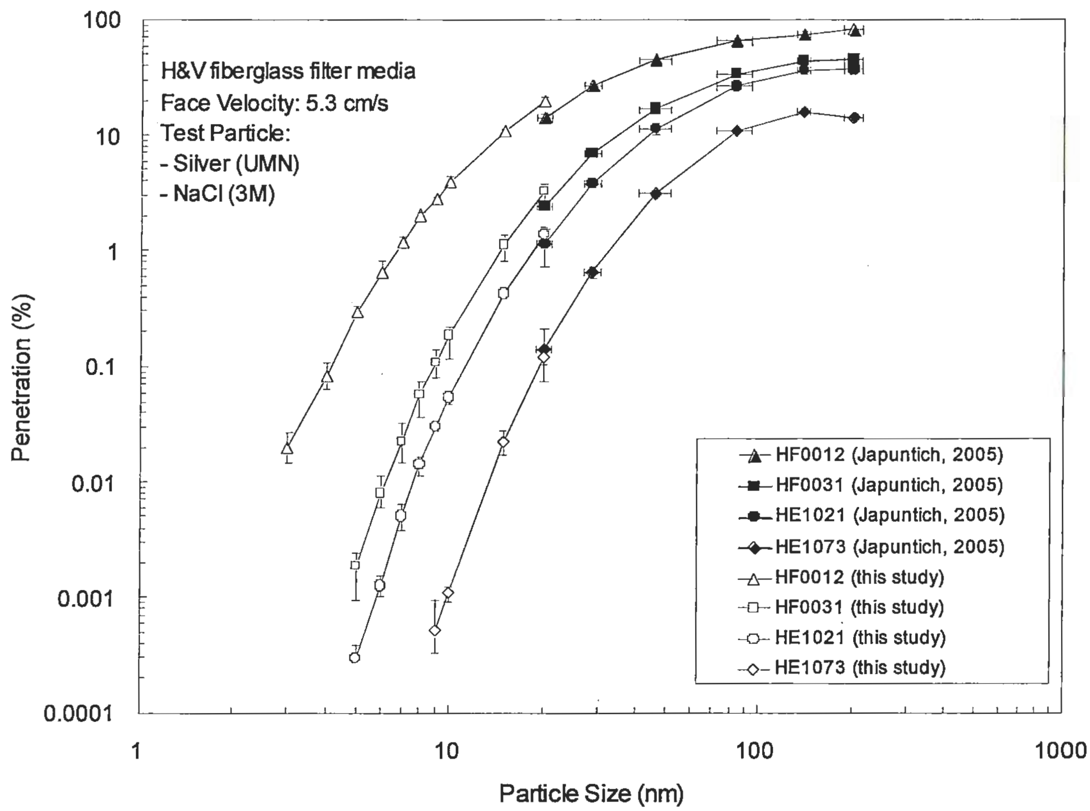


Fig. 10. Comparison of test results with other study for H&V fiberglass filter media