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Original Article

Feasibility study on the application of electrospun nanofiber webs for the air sampling of crystalline silica

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Abstract: The aim of the present study was to first fabricate an electrospun PVC nanofiber web and then assess its applicability in sampling and measuring the concentration of airborne crystalline silica by comparing analysis results with a commercial PVC membrane filter under different ranges of airborne silica concentration. A filtration performance comparison was also made between an electrospun PVC web with nano-sized fibers and a commercial PVC membrane filter. Overall, the measured concentration of silica by the electrospun webs was 1.022 times higher than that of the commercial PVC filter in all studied ranges of silica concentration and the nanofiber media had higher filtration efficiency and lower pressure drop compared to the PVC membrane filter. This can be considered to be due to the lower fiber diameter and greater porosity (obtained from the 2D SEM image) of the electrospun nanofiber webs. This makes them suited for air pollutant sampling and determining its airborne concentration.

Key words: Nanofiber web, PVC filter, Air sampling, Airborne silica, Electrospinning, Filtration

Introduction

The use of chemical substances in the work environment is an inevitable fact across the world and is increasingly becoming a health issue[1)]. Among the various kinds of aerosol that may be released within the work environment, silica dust (silicone dioxide) is known to be a very hazardous occupational agent. The International Agency for Research on Cancer (IARC) classifies crystalline silica dust as a class 1 carcinogen[2)]. The risk of exposure to silica dust is present in many workplaces including metal forging, mining, painting, ceramics and tiles, casting, and insulation[3)].

Identifying and controlling harmful chemical hazardous agents in the work environment is considered a part of the responsibilities of industrial hygienists. In the detection,

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measuring, and controlling of risks associated with airborne chemical pollutants in occupational environments, there is a stage referred to as the "sampling"[4]. In this regard, the National Institute for Occupational Safety and Health (NIOSH) has guidelines for the monitoring of airborne chemical substances in workplaces[5].

One of the common methods applied in the sampling of airborne particles is the use of membrane filter[6]. The widespread use of filter media is due to lower costs compared to other air sampling techniques, ease of sample collection, the ability to store samples for long periods before decomposition, and the ability to sample gases and vapors by impregnating the filter surface with absorbent solutions. The parameters involved in the selection of the filter include filter material (e.g., MCE, PTFE, PVC, …), nominal value of pore size (e.g., 0.45, 0.8 µm, ...), type of aerosol to be sampled, maximum allowed loading of contaminant on the filter, air temperature, air humidity, filter pressure drop and method of analysis[6, 7].

The recommended filter media used in the sampling of airborne crystalline silica is the polyvinyl chloride (PVC) membrane filter[8]. The PVC filter is commercially available in 0.5mµ, 0.8 mµ, and 5mµ pore sizes. PVC filter is useful for determining crystalline silica (named silica, here) in respirable dust samples by IR method. PVC filters are hydrophobic, have non-oxidizing surfaces, do not contain any silica, produce very little ash, and have a low net weight (during gravimetric weighing)[6, 9]. The use of pre-weighed PVC filters placed inside a holder along with a backing plate is a common practice for air sampling of silica. The sampling duration may vary depending on the type of holder used and the time required to reach the minimum sample volume (400 to 1,000 liters) determined in the methodology while considering the flow rate (2 to 4 lit/min) and it may vary depending on the circumstance in which the dust is sampled. Once the samples are prepared according to the chosen method (such as NIOSH 7602), they are analyzed using an infra-red spectrometry device equipped with a dual ion beam sputter or a Fourier transform device with a resolution of 4 cm^{-1} or higher[8].

Today, extensive research is being conducted on the use of nanotechnology in various fields with new applications being discovered for both everyday life as well as in industries. Nanofibers used as nano-objects with two similar nanosized outward dimensions and a considerably larger third dimension have characteristics that distinguish them from other one-dimensional structures[10].

Nanofibers can have a diameter ranging from 10 nm to 100 nm (in some cases as high as 500 nm) which enables them to have a high specific surface area, higher surface to volume ratio (1,000 times greater than that of conventional microfibers), higher surface flexibility, and great mechanical properties (such as improved tensile strength). These structures have flexible fibers where other materials can attach themselves to their pores making them a suitable host for these materials. Various materials can be used to fabricate nanofibers including natural and artificial polymers, carbon based materials, as well as compound and semiconducting materials[10]. Nanofibers can be manufactured using various techniques such as drawing, template synthesis, phase separation, self-assembly and electrospinning. Among them, solution electrospinning is common and widespread, with needle-based, needle-less and centrifugal approaches already being expanded and commercialized[11].

In the needle-based electrospinning method, a high-voltage field is applied to a droplet of polymer solution protruding from the tip of an injection syringe needle. A collector is placed at a specific distance from the tip of the needle and is either connected to ground or has an opposite charge in relation to the needle. If the electrical field between the needle and collector has enough potential to overcome the droplet's surface tension, a jet (projectile) is formed. If the solution is viscous, the jet can be elongated to form a very thin filtration medium[12, 13].

The morphological characteristics of electrospun nanofibers depend on many parameters including the conductivity, viscosity, and surface tension of the solution as well as process parameters such as the distance between the needle and collector, the applied voltage, and the rate of injection[14]. The filtration performance of nanofiber media has been evaluated in numerous studies where nanofibers have proven to be as effective as or even better than most HEPA filters in their collection efficiency while also causing less pressure drop[15, 16]. Ahn *et al.* created electrospun nylon 6 nanofibers with a diameter between 80 nm and 200 nm at various grammages[17]. They showed that at a basic weight between 5.75 g/m^2 and 10.75 g/m^2, it is possible to create filters with an air filtration performance comparable to that of HEPA filters[17].

Despite the proven performance and efficiency of nanofibers in capturing airborne particles, the applicability of this technology in the collection and sampling of airborne particles for determining the concentration of pollutants in the air has seldom gained attention in environmental and occupational studies. Indeed, extensive research is currently being undertaken on the use of nanofibers as air filter media for controlling air pollution or for producing face

masks as personal protection equipment, leading to the creation of many commercial products. However, less attention is paid to the applicability of nanofiber media in the capturing and sampling of airborne pollutants for determining contaminant concentrations in environmental and occupational exposure studies. The aim of the present study is to first fabricate an electrospun PVC nanofiber web and then assess its applicability in sampling and measuring the concentration of airborne crystalline silica by comparing the analysis results with a commercial PVC membrane filter under various ranges of airborne silica concentration. A filtration performance comparison will also be made between an electrospun PVC web with nano-sized fibers and a commercial PVC membrane filter suggested by NIOSH method.

Materials and Methods

Materials

The PVC-1S6532 polymer purchased from Arvand Petrochemical Co. (Iran) (molecular weight of 62.50 g/mol (per unit) and a density of 1.3 g/cm^3 to 1.45 g/cm^3) was used to create the nanofibers. The dimethylformamide (DMF) solvent from Merck (Germany) (molecular weight of 73.09 g/mol and a purity of higher than 99.8 %) along with the tetrahydrofuran (THF) solvent from Merck (Germany) (molecular weight of 72.11 g/mol and a purity higher than 99.8) were prepared at a 1:1 ratio to provide different concentrations of the PVC solution. In order to draw the calibration curve for silica analysis, the quartz standard code 7536 from Proanalysi (Norway) (purity of 99%) was purchased along with acetone from Merck (Germany) (molecular weight of 58.08 g/mol and a purity higher than 99.8%). The PVC membrane filter (nominal value of pore size 5 µm, 25 mm - SKC, Inc.; United States) was obtained to be compared with the results of air sampling of the electrospun nanofiber webs. KBr powder (code 104905) from Merck (Germany) (molecular weight of 119.01 g/mol and a purity of higher than 99.5%) was used in the composition of the pellet inside the Fourier-transform infrared spectroscopy (FTIR).

Fabrication of the Nanofiber Web

The materials used to produce the electrospinning solution include the PVC polymer, DMF, and THF. Based on the optimal conditions of electrospinning obtained according to previous study of the authors[18], the PVC/DMF/THF solvent was prepared with a concentration of 11 and 12 wt%. To achieve homogeneity, the solvent was heat stirred at room temperature (up to 30°C) for 3 to 6 hours. The PVC powders were dissolved inside the THF/DMF solvent at a 1:1 ratio[19].

The details of the preliminary research and the optimization of the electrospinning parameters (concentration, voltage, distance and duration) via the Design-Expert software solution for fabricating PVC nanofibers to be used in the sampling of airborne crystalline silica has been presented elsewhere (Project Number: 19854, ethics committee approval ID: IR.SBMU.PHNS.REC.1398.049)[18]. The nanofibers were produced using the needle-based solution electrospinning technique (Fanavaran Nano Meghyas, ES2000; Iran). The parameters used in the electrospinning process are presented in Table 1. The web numbers presented in Table 1 are identical to the number given to the experimental runs within the Design-Expert software in the optimization study; these three nanofibers were selected according to their high filtration performance, good appearance features such as strength and ease of use from the user's point of view, etc. The remaining parameters included temperature of 25°C, a collector covered with a polypropylene spunbond layer, injection rate of 2 ml/h, a 5 ml syringe, a 18 gauge needle (internal diameter of 0.84 mm), and a nozzle scanning rate of 300 mm/minute plus a drum rotation speed of 700 rpm.

Structural Properties of the Nano-Web

Images were taken from the electrospun nanofibers using a scanning electron microscope (SEM) (TE Scan Vega, Czech Republic). The images were taken at 5 different magnifications (×625; ×1,250; ×5,000; ×10,000 and ×20,000) with fiber diameters determined using the Image J software (National Institutes of Health, USA); around

Table 1. Electrospinning parameters used in nanofiber fabrication

Web No.*	Applied Voltage (kV)	Electrospinning Distance (cm)	Solution Concentration (wt%)	Electrospinning Time (hr)
4	20	12	12	2
12	20	12	11	2
17	17.50	13.50	11	3

*The web numbers are identical to the number given to the experimental runs within the Design-Expert software in the optimization study

50–100 measurements were taken from random fibers in the studied magnification[12].

In order to calculate the porosity (here, it is actually the area ratio from the 2D SEM image) of the images taken from samples, the SEM image analysis algorithm was used via the MATLAB software (Mathworks, v.7)[12]. Fourier Transform Infrared Spectroscopy (Rayleigh WQF 510 (China)) was conducted for the nanofibers for identifying the surface functional groups present on the nanofibers. A Caliper (ASIMETO 307-56-3 6" ABS; Hong Kong) has been used to measure thickness of the nanofiber webs.

Measurement location

The casting section of an automobile part manufacturing plant was chosen as the location for air sampling, where the existence of silica had previously been proven. The type of materials used in this section of the plant included crystalline silica, casting sand, ferroalloys, scrap metal, and refractive materials[20]. According to Kakui *et al.*, the core room, casting room, smelting room, and shot blasting rooms are potential sites for silica contamination[21].

Leveling the Silica Concentration

The silica concentration within the studied workplace was leveled according to both pilot research and the annual periodic monitoring reports considering the Threshold Limit Values (TLV) for crystalline silica exposure. Air samples for the pilot study were taken in compliance with the revised NIOSH 7602 method[22, 23]. The location for five ranges of airborne silica concentration was determined. The airborne silica concentration was leveled according to the guidelines suggested by the NIOSH and was based on TLVs ± 25[24].

Measurement method

Determining the Concentration of Airborne Crystalline Silica

Environmental air samples taken were according to the revised NIOSH 7602 method[22, 23] at different ranges of airborne silica concentration. For the sampling, a personal sampling pump (SKC AIRCHEK SAMPLER 224-44XR, USA) was first calibrated using a rotameter (Platon-NG) and a soap bubble flow meter. The 25-mm web was placed inside the desiccator for 24 hours before air sampling. Once the web inside the holder was weighed with an accuracy of 0. 1 mg (Sartorius, SECURA 225D-1S, Germany), it was transferred to the cyclone (cyclone SKC 225-01-02, USA/UK-5 µm cut-off point) and connected to the sampling pump. Sampling was carried out at a flow rate of 2.5 l/min and a constant duration to obtain an air sampling volume of 400 to 1,000 liters. Once sampling was done, the web was placed inside the desiccator for 24 hours (the room temperature, relative humidity was ~52%). Then, the secondary weight of the filter was measured using the calibrated balance. The PVC and electrospun filter media were used for air sampling. The number of samples was based on the Eq. 1:

[Five (level of silica concentration) × three (repetition) × three nanofiber webs + one PVC filter for each set of nanofibers webs] + (four control samples) = 60 + 4 = 64 (Eq. 1)

The control samples have been taken according to the suggested calculation in NIOSH 7602 method. There were five levels of silica concentration (0.5, 1, 2, 5, 10×TLV). In addition, there is one PVC filter for each set of the three NFs. For sampling, the personal sampling pumps were used for three sets, each sets containing four webs (web 4,12,17 and PVC). In each step of the sampling procedure, dry air temperature, relative humidity, and atmospheric pressure were measured for correcting the volume of air sampling using the anemometer (Benetech GM8910; USA). In order to prepare the samples, the web containing the sample was placed inside a crucible with 200 mg of potassium bromide added to the web so as to cover the entire surface of the web as well as the particles. Then, the crucible was placed inside a muffle furnace (HORST UHLING KG; Type U 24/St; 220v; 1,200w), where the temperature was raised from room temperature to 600°C during a 4-hour period. Once the sample cooled off, it was homogenized inside the crucible. The sample was then placed inside a 13 mm metal mold and pressurized to 20 MPa under a press to from a pellet. The pellets were scanned and their contents were measured at 825–711 nm and 400–4,000 cm^{-1} using through Infra-Red Fourier transform spectrometry (Rayleigh WQF 510A, China). The FT-IR software was used to calculate the surface area of the crystalline silica peak[22, 23].

In order to draw the calibration curve, standardized silica samples were made. For this purpose, around 4mg of high purity standard silica powder (Particle size: 0.011 µm, Sigma-Aldrich 381276; USA) was added to 4 ml of acetone solvent and placed on a magnetic mixer in a suspended condition. The volumes required were taken using a micro pipette from a range of 15 µl to 160 µl. This was poured onto the PVC which had 200 mg of potassium bromide added to it earlier. Once the acetone dried, the samples were placed inside a muffle furnace for 4 hours with the temperature raised from room temperature to 600°C. After

cooling, the samples were homogenized inside a crucible and transferred to a 13 mm mold and pressurized to 20 MPa under a press to form a pellet. The pellets were then scanned and their contents measured at 825–711 nm and 400–4,000 cm^{-1} using the FT-IR spectrometry device to obtain the calibration curve. The concentration of the collected silica was calculated for each sample using the calibration curve and the corresponding peak surface area.

In order to estimate the limit of detection (LOD) and the limit of quantitation (LOQ) of the determination of silica, the PVC filter was analyzed.

Stability of Samples

The stability of silica samples collected by the nanofiber web was determined by comparing the immediate and long-term analysis results. Two sets of samples were taken with six samples in each set. The first set was immediately analyzed, while the second set was analyzed after seven days in storage. The mean concentration of each set may have up to 10 % difference[24].

Accuracy

In order to determine the repeatability of results obtained from the nanofiber web, three sets of samples (at 0.5, 1, and 2 times the TLV) were taken with each set containing six samples. The coefficient of variation (CV) obtained from the sampling must be lower than 0.105[24].

Validity

In order to determine the similarity between the results of the two sampling filters (PVC nanofiber web and membrane filter), three sets of sampling were taken (at 0.5, 1, and 2 times the TLV) with six samples in each set. The mean concentration silica measured by other nanofiber webs must be within a 10% difference of the PVC membrane filter for all three test levels[24].

Testing Filtration Efficiency

In order to assess the initial pressure drop and filtration efficiency, Di-Ethyl-Hexyl-Sebacat (DEHS) particles with a size of 0.3 μm or larger were used inside the filter test rig of the Fanavaran Nano Meghyas Company (FNM filter test, FT150EG, Iran).

The net effective filtration area was 14.3 cm^2 and the airflow rate was adjusted at a rate to create a face velocity of 10 cm/s. All tests were performed at an air temperature of 20 to 25°C, a relative humidity of 25% to 50%, and an atmospheric pressure of 101.2 kPa. The filtration efficiency was determined by calculating the numerical concentration and size distribution of particles in the up and downstream of the media using a particle counter (FNM filter test rig, FT150EG; Iran) with sampling time of two minutes and the flow rate of 28 liters per minutes. The pressure drop was determined using a differential manometer. In order to calculate the percentage of uncertainty, a confidence interval of 95% was considered along with a degree of freedom equal to 5 and an n value = 6 (Six experimental runs were performed in the trial)[25]

The filtration efficiency was calculated for a specific size range (Ei(%)) using the Eq. 2[26]:

$$E_i(\%) = \left[1 - \frac{n_i}{N_i}\right] \times 100 \text{ (Eq. 2)}$$

In the above equation, n_i is the number of particles in the size range "i" at the downstream of the media and n_i denotes the number of particles within the size range "i" at the upstream of the media[26].

A coefficient of variation (CV) below 5% is an indication of acceptable precision. The penetration percentage of the web is equal to 100 subtracted by filtration efficiency percentage. The number of tested samples was determined based on the Eq. 3:

$$\text{[Four (one PVC filter and three nano-fiber webs) × six (set of tests)]} = 4 \times 6 = 24 \text{ (Eq. 3).}$$

The quality factor (QF) of filter media which is a measure of the filter's quality was calculated according to Eq. 4[26].

$$QF = -\frac{1n(1-E/100)}{\Delta P} \times \text{(Eq. 4)}$$

Where, E: efficiency (%) and ΔP: *pressure drop* (*Pa*).

The quality factor is the ratio of filtration efficiency to pressure drop and it is generally desirable to have a filter with high filtration efficiency and low-pressure drop. Thus, a higher quality factor means a higher filtration performance.

Ethics approval

Ethical approval for this study was obtained from School of Public Health & Neuroscience Research Center, Shahid Beheshti University of Medical Sciences (IR.SBMU.PHNS.REC.1398.008).

Results

Determining the Concentration of Airborne Crystalline Silica

Table 2 compares the mean concentration of crystalline

Table 2. The mean concentration of airborne crystalline silica (mg/m^3) measured by FT-IR in different webs

Pollutant Load	Filter media								
	PVC filter vs. NF* web 4		PVC filter vs. NF web 12		PVC filter vs. NF web 17		PVC filter vs. Mean NF webs		
	PVC	Web 4	PVC	Web 12	PVC	Web 17	PVC	NF	NF/PVC
2x Lower Than TLV	0.007	0.012	0.008	0.012	0.008	0.013	0.007	0.012	1.652
TLV	0.021	0.022	0.021	0.023	0.020	0.024	0.020	0.023	1.136
2x Higher Than TLV	0.039	0.040	0.042	0.043	0.045	0.048	0.042	0.044	1.043
5x Higher Than TLV	0.127	0.128	0.132	0.132	0.138	0.138	0.132	0.133	1.004
10x Higher Than TLV	0.270	0.270	0.272	0.272	0.275	0.275	0.272	0.272	1.000
Mean	0.093	0.094	0.094	0.096	0.097	0.100	0.095	0.097	1.0216
NF/PVC	1.017		1.022		1.026		1.022		

*NF: Nanofiber

silica measured with FT-IR method collected by the studied media. Considering the mean number of repetitions for each experimental run, overall, the measured concentration of silica by the electrospun webs was 1.022 times higher than that of the commercial PVC filter in all ranges of silica concentration. Among the three nanofiber webs, the measured silica using the web 17 had more silica concentration than the other two, where the measured concentration of silica was 1.026 times higher than that of the commercial PVC filter.

The LOD and LOQ were calculated using the standard deviation (0.00031) of the measurement and the slope of the calibration curve (0.0189). LOD of 0.049 µg and LOQ of 0.162 µg were obtained[3]. Based on the calculations of stability of samples, the silica concentration difference between the nanofiber webs and PVC membrane immediately analyzed was 0.32%, while the difference was 0.34% for analyzing after seven days. In case of accuracy, the CV obtained for the nanofiber web was 0.097, which was lower than 0.105. The sampling performance of the nanofiber media was higher than that of the commercial PVC membrane filter for all ranges of silica concentration, and thus the validity of results was calculated to be 104%.

Filtration Performance

The filtration performance of the media is outlined in Table 3 for various particle sizes. Overall, the nanofiber media had higher filtration efficiency and lower pressure drop compared to the PVC membrane filter, which lead to a higher quality factor for all particle sizes. On average, the nanofiber web 17 had the highest efficiency for all particle sizes and the lowest pressure drop, while the commercial PVC filter had the highest pressure drop and the lowest filtration efficiency plus quality factor. A comparison of mean filtration efficiency, pressure drop, and quality factor in the removal of particles sized 0.3 µm to 10.0 µm is presented in Fig. 1 for all studied media.

The three nanofiber webs (177.66 Pa) had lower pressure drop compared to the commercial PVC filter (204 Pa). The electrospun webs had a higher filtration efficiency (92.66%) for all particle sizes compared to the commercial PVC filter (90.16%). The web 17 had the highest filtration efficiency among the three studied media.

Structural Properties of the Nanofiber Web

The fiber diameter of the produced webs is presented in Table 4. The fibers had a mean diameter of 277.88 ± 0.09 nm, with the lowest diameter belonging to the web 17 (256 ± 0.07 nm). Morphologically, if the ratio of the fiber diameter's standard deviation (SD) to its mean diameter is less than 0.3, it is referred to as a "uniform" or "smooth" fiber[27]. According to this definition, the webs from the webs 17 and 12 had uniform fibers. The SEM images (at 5,000x) of the various nanofiber webs and the commercial PVC membrane filter are shown in Fig. 2. SEM images indicates the particles trapped inside the electrospun nanofibers after the

Table 3. Filtration performance of the webs

Particle Size (μm)	Parameter		Nanofiber web 4	Nanofiber web 12	Nanofiber web 17	PVC membrane filter
0.3	Initial Efficiency (Ei) (%)	Mean (±SD)	81.10 ± 1.04	83.10 ± 1.32	88.10 ± 1.14	80.10 ± 1.09
		Uncertainty (U) (%)	1.09	1.38	1.19	1.14
		Variation Coefficient	1.28	1.59	1.29	1.36
	Penetration (%)		18.90	16.90	11.90	19.90
	Quality Factor (Pa^{-1})		0.019	0.020	0.024	0.002
0.5	Initial Efficiency (Ei) (%)	Mean (±SD)	85.10 ± 1.35	88.10 ± 1.29	90.10 ± 1.26	83.10 ± 1.21
		Uncertainty (U) (%)	1.41	1.35	1.32	1.26
		Variation Coefficient	1.58	1.46	1.40	1.45
	Penetration (%)		14.90	11.90	9.90	16.90
	Quality Factor (Pa^{-1})		0.022	0.024	0.027	0.002
1.0	Initial Efficiency (Ei) (%)	Mean (±SD)	91.10 ± 1.11	92.10 ± 1.01	94.10 ± 1.15	91.10 ± 1.45
		Uncertainty (U) (%)	1.16	1.05	1.20	1.52
		Variation Coefficient	1.21	1.09	1.22	1.59
	Penetration (%)		8.90	7.90	5.90	8.90
	Quality Factor (Pa^{-1})		0.028	0.029	0.033	0.003
2.5	Initial Efficiency (Ei) (%)	Mean (±SD)	93.00 ± 0.86	95.00 ± 0.01	96.00 ± 0.81	92.00 ± 0.63
		Uncertainty (U) (%)	0.90	0.01	0.84	0.66
		Variation Coefficient	0.92	0.01	0.84	0.68
	Penetration (%)		7.00	5.00	4.00	8.00
	Quality Factor (Pa^{-1})		0.031	0.035	0.037	0.003
5.0	Initial Efficiency (Ei) (%)	Mean (±SD)	97.00 ± 0.70	98.00 ± 0.58	98.00 ± 0.95	97.00 ± 0.50
		Uncertainty (U) (%)	0.52	0.99	0.60	0.73
		Variation Coefficient	0.51	0.96	0.59	0.72
	Penetration (%)		3.00	2.00	2.00	3.00
	Quality Factor (Pa^{-1})		0.041	0.046	0.046	0.005
10.0	Initial Efficiency (Ei) (%)	Mean (±SD)	99.00 ± 0.08	100.00 ± 0.00	100.00 ± 0.00	98.00 ± 0.05
		Uncertainty (U) (%)	0.08	0	0	0.05
		Variation Coefficient	0.08	0	0	0.05
	Penetration (%)		1.00	0.00	0.00	2.00
	Quality Factor (Pa^{-1})		0.054	0.135	0.135	0.006
Mean Initial Efficiency (%)			91.05	92.66	94.33	90.16
Mean Initial Penetration (%)			8.95	7.34	5.67	9.84
Mean Quality Factor (Pa^{-1})			0.013	0.014	0.019	0.011
Mean Initial Pressure Drop (Pa)			192	187	154	204
Most Penetrating Particle Size (MPPS) (μm)			0.3	0.3	0.3	0.3

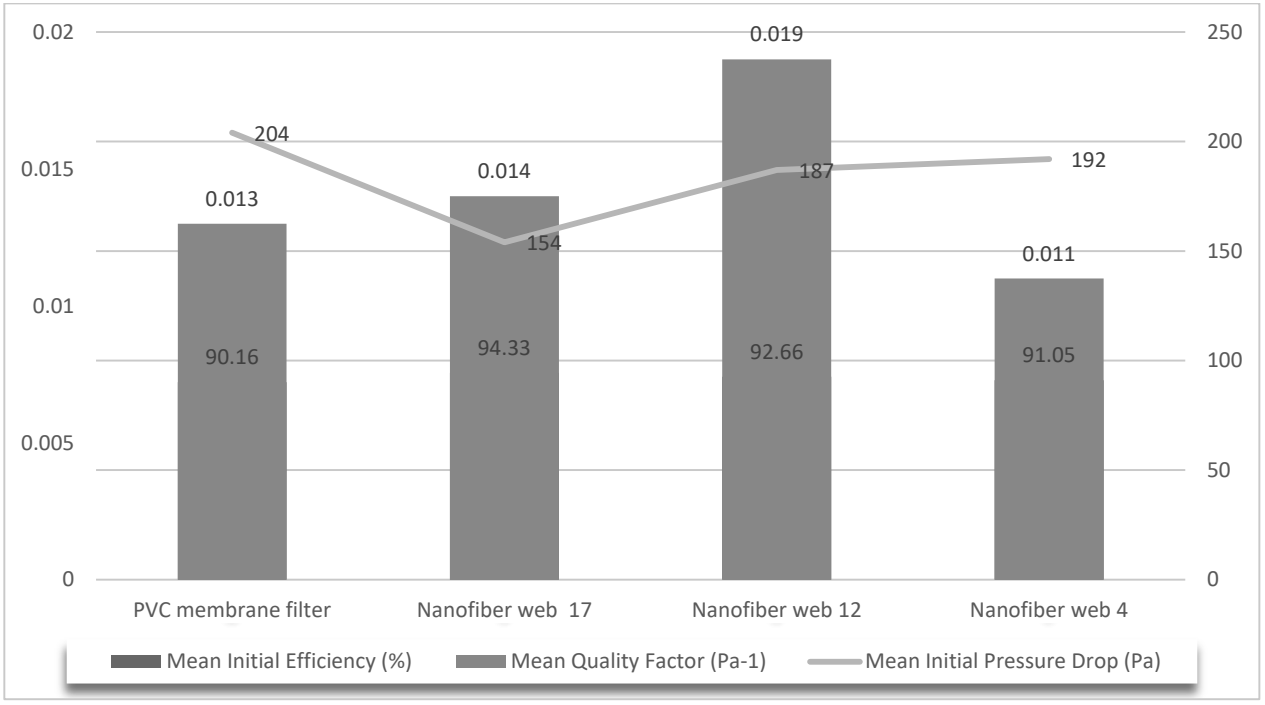
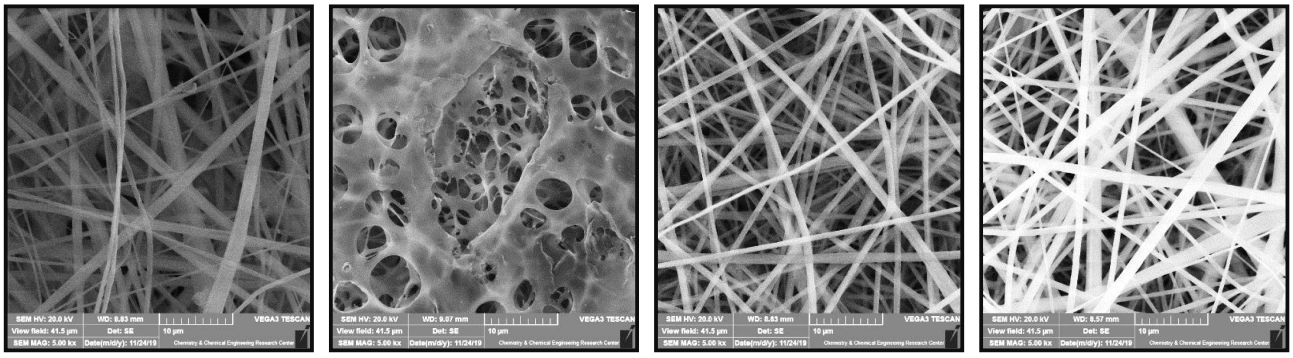


Fig. 1. Comparison of mean efficiency, pressure drop and quality factor of the studied webs for removing particles sized 300–1,000 nm.



Nanofiber web 4 Commercial PVC Filter Nanofiber web 17 Nanofiber web 12

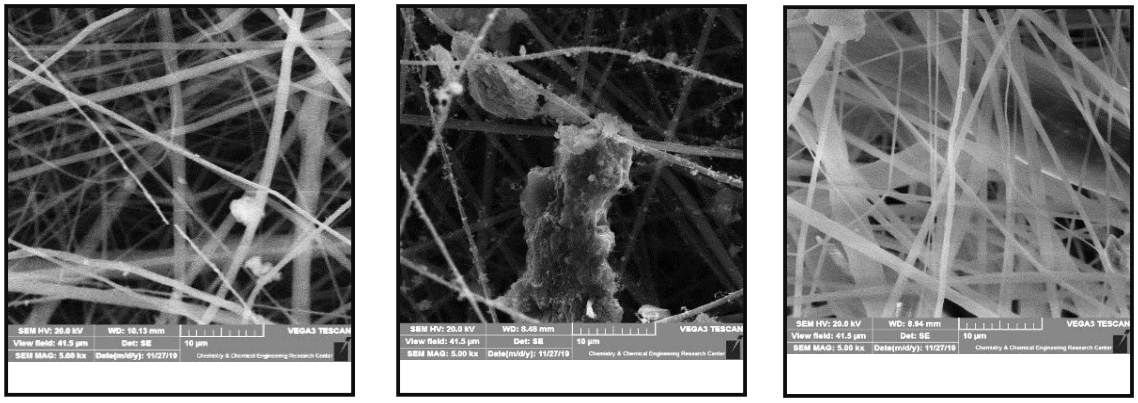
Fig. 2. SEM images from the studied filter media.

air sampling (Fig. 3). The size of a microspore on a fiber of the media was calculated to be 30.1% for the web 4, 28.9% for the web 12, 28.48% for the web 17 (Table 4), and 25.1% for the PVC membrane filter.

Fig. 4 displays the FTIR spectrum of the nanofiber media. Peaks at 2,972 cm^{-1} and 2,910 cm^{-1} indicate asymmetrical stretching vibration of CH2 within the PVC polymer. The peak of the upper wave indicates asymmetrical stretching of the C-H bond, while the lower peak reveals symmetrical stretching of the C-H bond. The peaks at 1,400 cm^{-1} are related to the aliphatic bent bond between C-H. The peak at 1,250 cm^{-1} is related to the bent bond between C-H situated near CI. The C-C stretching bond of the PVC backbone chain has occurred within the 1,000–1,100 cm^{-1} range. The peaks within the 600–650 cm^{-1} range correspond to the gauche bond between C–CI[28].

Discussion

The purpose of this research was to assess the applicability of an electrospun PVC nanofiber web in sampling and measuring concentration of airborne crystalline silica by comparing the analysis results between the fabricated nanofiber webs and the PVC membrane filter suggested by NIOSH method. Based on our findings, the concentration of silica collected by the nanofiber web was higher than that of commercial PVC filter for various ranges of airborne silica concentration. On average, the silica concen-



Nanofiber web 17 Nanofiber web 12 Nanofiber web 4

Fig. 3. SEM images showing trapped particles within the nanofiber webs after the air sampling.

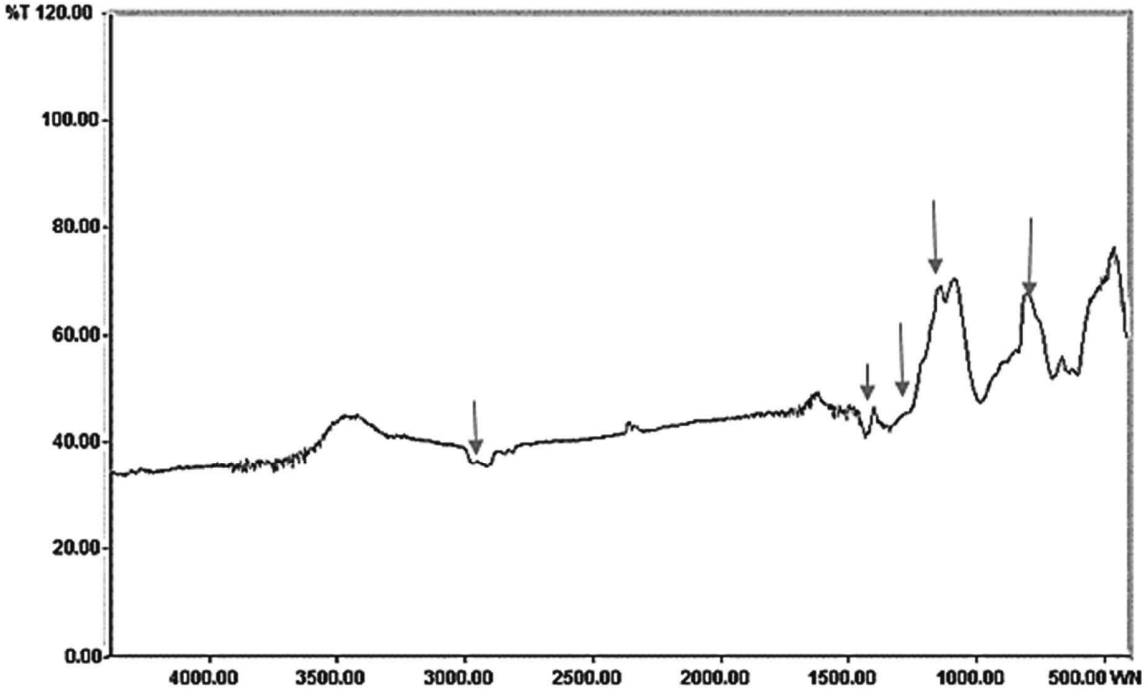


Fig. 4. FTIR spectrum of the PVC nanofiber web#17.

tration which was measured using nanofiber media was 1.022 times higher than that by commercial PVC filter. The ratio of collected silica by the nanofiber web to PVC filter was higher for lower ranges of airborne silica concentration, but it had a downward trend as the range of silica concentration increased. In general, the nanofibers have been shown to be better able to removing smaller particles from airstream than microfibers; therefore, in present study, nanofiber webs presented a higher ability in sampling concentration of airborne silica under lower ranges of silica concentration that may have a greater number of small particles.

As the results of the filtration test showed, the mean filtration efficiency of the nanofiber media in the removal of artificial dust smaller than 5 μm had a greater difference with that of the PVC membrane filter.

In all nanofiber webs (Table 4), the mean diameter of the fiber was equal to 277.88 ± 0.09 nm. The mean coefficient of variation(CV) in all three experiments was 0.32. Considering the commercial nature of the PVC filter and its press type, it was not possible to find any fiber to measure its diameter. According to the classic filtration theory, efficiency has an inverse relationship with fiber diameter[29]. Fibers with smaller diameters have a larger surface area, and a

Table 4. Structural Properties of the Nanofiber Web

Web No.	Fiber Diameter (nm)			Thickness (mm)	Porosity (%)
	Mean(nm)	Standard Deviation	Coefficient Variation		
4	294	12.00	0.44	0.124	30.10
12	281	0.06	0.23	0.126	28.90
17	256	0.07	0.29	0.125	28.48
Mean	277.88	0.09	0.32	0.125	29.16
PVC		----		0.125	25.10

smaller porosity, causing increased filtration efficiency. Fibers with a larger diameter, on the other hand, are usually bulkier and porous while having higher air penetration and lower pressure drop[30].

The mean porosity (here, it is actually the area ratio from the 2D SEM image) obtained for the nanofiber webs was higher than that of commercial PVC filters. The mean porosity of the nanofiber webs was 29.16%. Due to the voids within the nanofiber media resulting from the electrospinning process as well as the lack of an industrial press, the nanofiber webs are more porous compared to the commercial PVC filter. Greater porosity usually can provide more dust holding capacity, resulting in enhanced filtration efficiency.

According to the classic filtration theory, pressure drop in constant flow regimes had an inverse relationship with the square of the fiber diameter. Meanwhile, the increase in pressure drop had a more gradual slope with smaller nanofiber diameters due to the slip effect[31]. According to Brown, increased pressure drop was observed at lower fiber diameters even in slip regimes[32]. It has been proven that slip regimes occur around the nanofiber when air is passing through. This is because the fiber diameter is close to the size of the mean free path of gas molecules (for instance 65 nm for air at standard temperature and pressure). In a slip flow, the air velocity at the surface of the fiber is considered to be greater than zero[33].

Regarding the Table 3, the nanofiber webs had a higher quality factor (0.015) compared to the commercial PVC filter (0.011). Considering the lower porosity (aperture obtained from 2D images) of the commercial PVC filter compared to the three nanofiber webs, its pressure drop has been higher than others. The slip flow within the nanofiber has been existed which can lead to lower pressure drop and higher filtration efficiency[34].

Wang *et al.* showed that by increasing the concentration of the electrospinning solution from 7% to 13%, the mean fiber diameter increased form 175 nm to 558 nm leading to a reduction of filtration efficiency from 98.89% to 40.80%[35]. They attributed it to the increased bubble point diameter of the nanofiber web[35]. This also reduced pressure drop from 53 Pa to 3 Pa and resulted in an increased quality factor from 0.086 to 0.175. Wang *et al.* stated that these characteristics are important factors in making the fiber economically and commercially viable[35]. The electrospun nanofiber web 17 was fabricated at a lower applied voltage, lower concentration of solution, and greater electrospinning distance, giving it a lower diameter and lower porosity compared to the other two nanofiber webs. The mean diameter of the fiber depends on the electrospinning parameters[36]. The applied voltage affects the fiber diameter but this is also influenced by the concentration of the solution and the distance between the needle and the collector[10]. Generally, increasing electrospinning distance provides more time for the solvent to vaporize and thus results in a lower fiber diameter[37]. Many studies have stated that fiber diameter is greatly affected by the solution concentration and that a higher concentration leads to a larger fiber diameter due to increased viscosity and reduced elongation of the polymer jet[12]. Uspenskaya produced electrospun PVC nanofibers. The mean fiber diameter and the size distribution were determined to be 270–450 nm[38]. Comparing their study design with the electrospinning conditions and solution concentrations of the present study, it can be concluded that the mean fiber diameter obtained in the present study was within an average range of Uspenskaya's study.

The higher filtration performance of the web 17 can be attributed to its smaller diameter and lower porosity (obtained from the 2D SEM image) It is obvious that filtration efficiency increases as the fiber diameter is reduced, which is consistent with the theory of slip flow. In the case of a slip flow, the movement of the particles suspended in air is closer to the surface of the fiber, which increases the chance of them being captured through direct contact.

Conclusion

The present study compared the performance of electrospun nanofiber webs and commercial PVC filters in the sampling of airborne crystalline silica. The results showed that the electrospun nanofiber webs had a higher filtration performance (higher filtration efficiency and lower pressure drop) and were better able to collect the silica particles from the air stream compared to the PVC membrane filter. This can be considered to be due to the lower fiber diameter and greater porosity of the electrospun nanofiber webs. This makes them better suited for air pollutant sampling and determining its airborne concentration. The web 17 had the lower fiber diameter and porosity percent among the three fabricated webs, and so it has higher efficiency, lower pressure drop, and higher capture amount of crystalline silica.

Abbreviation List

CV	Coefficient of variation
DEHS	Di-Ethyl-Hexyl-Sebacat
DMF	Dimethylformamide
FTIR	Fourier-transform infrared spectroscopy
HEPA	High-Efficiency Particulate Air
IR	Infrared spectroscopy
LOD	Limit of detection
LOQ	Limit of quantitation
MCE	Mixed cellulose ester
NIOSH	National Institute for Occupational Safety and Health
PTFE	Polytetrafluoroethylene
PVC	Polyvinyl chloride
SEM	Scanning electron microscope
THF	Tetrahydrofuran
TLV	Threshold limit value

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Competing Interests

The authors have no competing interests to declare.

Author Contribution

SFD managed and planned the project. MJF contributed to the study design. MF, EAP and AK collected the data in the field. MF and ET analyzed the data. SF and MF were a major contributor in data interpretation, conclusion and writing the manuscript. All authors read and approved the final manuscript.

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