

## 2. Materials and Methods

### 2.1 Collection Efficiency Measurement

The experimental set up used for the evaluation of the collection efficiency of the NSC, is shown in Figure 1. A medical nebulizer (Salter 8900 Series Disposable Small Volume Jet Nebulizer; Salter Labs, Arvin, CA, USA) was used for the generation of the aerosols. Liquid solutions of sodium chloride (soluble) and suspensions of respirable crystalline silica (insoluble) were used. A diffusion dryer (model 3062, TSI Inc., Shoreview, MN, USA) was used downstream of the nebulizer for removal of water vapor. Crystalline silica aerosol was also generated from a dry powder using a fluidized bed aerosol generator (model 3400A, TSI Inc., Shoreview, MN, USA). The aerosol exiting the fluidized bed generator had a relative humidity of 60%. The Aerodynamic Aerosol Classifier (AAC; Cambustion Ltd, Cambridge, United Kingdom) was used to obtain classified near-monodisperse (in aerodynamic size) test aerosol above 25 nm diameter, while an Electrostatic Classifier (model 3080; TSI Inc., Shoreview, MN, USA) and a Nano-Differential Mobility Analyzer (model 3085; TSI Inc., Shoreview, MN, USA) were used to obtain smaller particle sizes. Aerosols generated by the nebulizer, were classified through the nano-DMA and the AAC, while for the crystalline silica particles generated by the Fluidized Bed, only the AAC was used. During the collection efficiency evaluation, a total flowrate of 1.2 L min<sup>-1</sup> was introduced into the NSC. The outlet of the collector was connected to an Ultrafine Condensation Particle Counter (model UCPC 3776; TSI Inc., Shoreview, MN, USA) to measure the number of particles that were transmitted throughout the collector. The UCPC required a total flowrate of 1.5 L min<sup>-1</sup>; thus, filtered, dilution air was added as make-up air to the aerosol stream exiting the collector. The same UCPC with the make-up air was also connected at the inlet of the NSC for

measuring the total aerosol concentration upstream of the collector. The collection efficiency was defined as,

$$\eta_c = 1 - \frac{N_{in} - N_{out}}{N_{in}} \quad (1)$$

where  $N_{in}$  ( $\text{cm}^{-3}$ ) corresponds to the total number concentration measured by the particle counter before the NSC inlet and  $N_{out}$  ( $\text{cm}^{-3}$ ) corresponds to the number concentration measured by the particle counter at the outlet of the NSC. The dilution by the make-up air is accounted for by being consistently applied to both number concentration measurements.

The collection efficiencies for different particle diameters and at different number concentrations were measured. Firstly, the effect of particle diameter on the NSC performance was compared at two initiator temperatures, 40 or 45 °C. Three temperature combinations for the initiator and the moderator were tested for the number concentration effect: 40 and 12 °C, 45 and 12 °C, and 45 and 25 °C.

## **2.2 Spot Sample Characteristics: Deposit diameter**

Polystyrene latex (PSL) nano and micro-spheres (Thermo Fisher Scientific, Waltham MA, USA) were used for studying the characteristics of the spot sample collected on the substrate. A broad size range of polystyrene spheres (20 nm-1900 nm) was generated, for examining potential particle size effects on the diameter of the spot sample. A Scanning Electron Microscopy (SEM) stub was positioned in the sample heater chamber of the collector, and an aluminum backed carbon tape (Ted Pella Inc., Redding CA, US) was placed on the surface of the stub, for the acquisition of superior SEM (Phenom XL Desktop SEM, Thermo Fisher Scientific, Waltham MA, USA) images

on a smooth surface with minimum uneven illumination effects. The ImageJ software (Schneider, Rasband, and Eliceiri 2012) was implemented for measuring the projected area of the accumulated particles depicted on the SEM images. The calculated spot deposit diameter ( $D_{90}$ ) corresponds to the diameter of the circle that contains 90% of the total projected area of the collected particles in the spot sample.

### **2.3 Spot Sample Characteristics: Deposit uniformity**

The spatial uniformity of the collected particle sample through the NSC was examined by employing Raman Spectroscopy. The Raman intensity obtained at different sampling locations, across the sample's diameter. For that, crystalline silica (Min-U-Sil@5) was collected on the warmed surface of a SEM stub, that was embodied in the NSC. The initiator temperature was set at 45 °C. Stepwise spectra were acquired every 0.1 mm across four different “paths” on the collected sample (horizontal, vertical, and two diagonal), starting from the edge of the sample, scanning across the sample's diameter until the opposite edge.

### **2.4 Calibration for Raman Measurement**

Test aerosols for Raman measurement were obtained using aerosolization of dry crystalline silica powder (Min-U-Sil@5; US Silica, Katy TX, USA) in a fluidized bed generator. The SEM stub's surface was cleaned with isopropyl alcohol before mounting into the sample chamber of the collector. During the particle collection, a piezo balance dust monitor (model 3520; Kanomax, Andover NJ, USA) was used to simultaneously quantify the aerosol mass concentration entering the NSC. The nominal analyte mass ( $m_p$ ), based on the inlet aerosol concentration entering the NSC was calculated as follows:

$$m_p = C_i t_c Q_c \quad (2)$$

where  $C_i$  is the mass concentration measured by the dust monitor ( $\text{mg cm}^{-3}$ ),  $t_c$  is the collection time (s) and  $Q_c$  is the NSC flowrate (equal to  $1.2 \text{ L min}^{-1}$ ).

For the Raman signal intensity acquisition, the portable i-Raman Spectrometer (i-Raman<sup>®</sup>; B&W Tek, Newark, DE, USA) was implemented. The maximum laser power and the laser spot diameter incident on the sample was 420 mW, and about 105 micrometers, respectively. The excitation wavelength was at 785 nm. An integration time of 30 s was used for this study. The characteristic peak for crystalline silica was observed at a Raman shift of  $465 \text{ cm}^{-1}$  for  $\alpha$ -quartz. The Raman calibration curves were constructed by using the area below the characteristic peaks and the particulate mass collected on the SEM stub.

Two calibration curves were extracted from the linear fit curves obtained from the experimental data, for two different initiator temperatures, 40 and 45 °C. The trendline equation derived from the calibration curves, is shown:

$$\frac{I_p}{t} = S^* \frac{m_p}{A_d} \quad (3)$$

where  $I_p$  is the Raman Intensity signal,  $t$  is the Raman integration time (s),  $m_p$  is the particulate mass collected ( $\mu\text{g}$ ),  $A_d$  is the deposition area ( $\text{mm}^2$ ) and  $S^*$  is the slope of the calibration curve.

## 2.5 Analytical Measurement Sensitivity

The calibration curve's slope ( $S^*$ ;  $\mu g^{-1} mm^2$ ) obtained here, can serve as the Raman spectroscopic analysis sensitivity. By assuming that the aerosol of interest and the analysis conditions remain identical when implementing different collection techniques and by using the measured sensitivity, the analytical measurement sensitivities of prevalent particle collection methods can be extracted and then be compared with the measurement sensitivity of the NSC.

The nominal particulate mass ( $m_p$ ;  $\mu g$ ) that is expected to be collected for subsequent spectroscopic analysis was calculated:

$$m_p = \eta_c Q C_{in} t_c \quad (4)$$

where the size-dependent collection efficiency of each of the collection technique applied is denoted by  $\eta_c$ , the aerosol-laden stream flowrate is denoted by  $Q$  ( $L \text{ min}^{-1}$ ), the aerosol number concentration is denoted by  $C_{in}$  ( $\mu g \text{ m}^{-3}$ ), and the collection time is denoted by  $t_c$  (min). From Equations (3) and (4), the following equation can be derived:

$$\frac{I_p}{t} = \frac{S^* \eta_c Q t_c}{A_d} C_{in} \quad (5)$$

By plotting the Raman signal intensity per unit integration time ( $I_p/t$ ; a.u.  $s^{-1}$ ) as a function of the aerosol concentration ( $C_{in}$ ;  $\mu g \text{ m}^{-3}$ ), the slope corresponds to the constant of  $S^* \eta_c Q t_c / A_d$ . This constant represents the analytical measurement sensitivity ( $S_c$ ;  $\mu g^{-1} m^3$ ):

$$S_c = \frac{S^* \eta_c Q t_c}{A_d} \quad (6)$$

Equation (6) can then be implemented for calculating the analytical measurement sensitivity of the NSC, Sequential Spot Sampler, the Aerodynamic Lenses, and the filtration. Table 1 shows the operating parameters of the NSC, the Sequential Spot Sampler, the Aerodynamic Lenses apparatus, and the filtration used for the calculation.

## 2.6 Poisson Counting Statistics of Fiber Concentration Measurement

Calculations were performed to compare Poisson counting statistics of fiber concentration measurement using the phase contrast microscopy (PCM; NIOSH Method 7400) for various collection methods, such as NSC, Sequential Spot Sampler and filter-based collection. The uncertainty ( $\sigma\%$ ) of the PCM fiber counting method can be calculated:

$$\sigma = \frac{1}{\sqrt{N}} \quad (7)$$

where  $N$  is the total number of fibers in the microscopy analysis area. The estimated sample collection time ( $t_c$ ) needed to achieve target counting uncertainty for measurement of 0.1 fiber/cm<sup>3</sup> ( $C_f$ ) using the NIOSH Method 7400 for various collection methods was calculated:

$$t_c = \frac{N A_d}{A_m C_f Q \eta_c} \quad (8)$$

where  $A_d$  is the spot deposit area of each collection technique and  $A_m$  is the microscopy analysis area. The recommended substrate area for microscopy analysis is 0.785 mm<sup>2</sup> (NIOSH 2019). The area of the spot sample from NSC was about 0.385 mm<sup>2</sup>, whereas the area over which the sample was collected using the 13 mm and 25 mm filters was 133 and 491 mm<sup>2</sup> respectively. For a substrate area for microscopy analysis of 0.385 mm<sup>2</sup> ( $A_m$ ), a fiber density on the substrate in the range of 260-1300 mm<sup>-2</sup> is recommended for optimum and unbiased counting ( $\sigma=4.5-10\%$ ). Table 1 shows the operating parameters of the aerosol collection techniques for calculation of the estimated uncertainty using Poisson counting statistics for phase contrast microscopy.

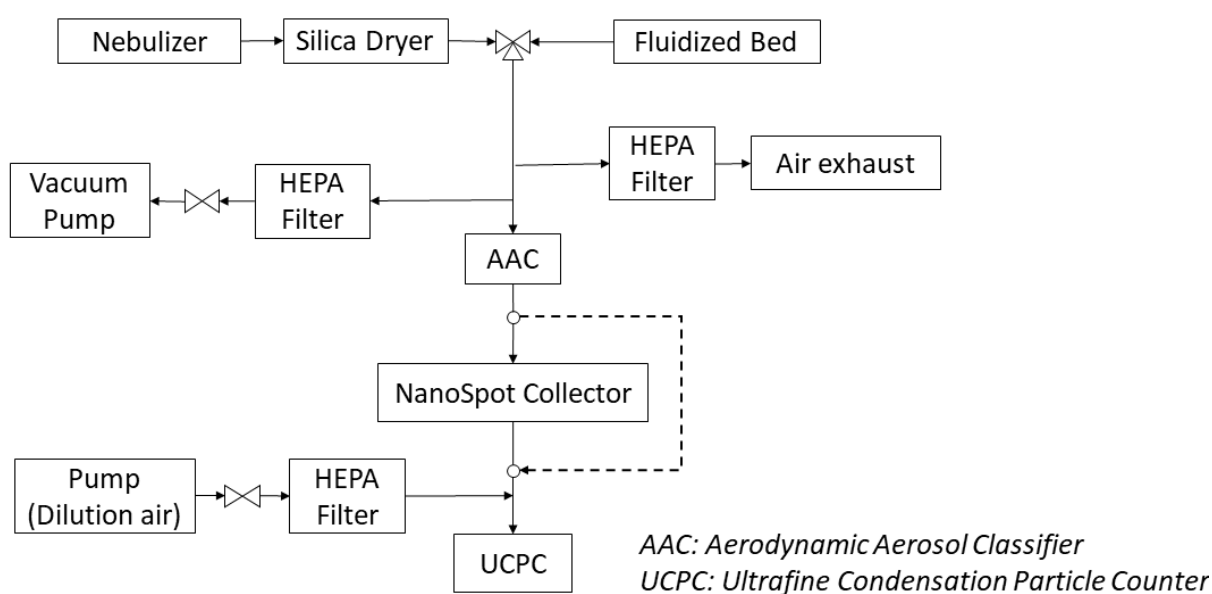


Figure 1. Schematic diagram of the experimental set-up for the characterization of the NanoSpot Collector. Same UCPC was used to measure inlet and outlet concentrations for transmission efficiency measurement.

Table 1. Operating parameters of aerosol collection techniques for calculation of the analytical measurement sensitivity for spectroscopic analysis and the estimated uncertainty using Poisson counting statistics for phase contrast microscopy.

<i>Collection technique</i>	<i>Collection Efficiency</i>	<i>Aerosol Sample Flow Rate (L min<sup>-1</sup>)</i>	<i>Spot sample diameter (mm)</i>
<b><i>NanoSpot™ Collector</i></b>	0.9	1.2	0.7
<b><i>Sequential Spot Sampler™</i></b>	0.95	1.5	1.0
<b><i>Aerodynamic Lenses<sup>a</sup></i></b>	0.3-1.0	0.108	0.37-22.67
<b><i>13-mm-filter</i></b>	1.0	2	13
<b><i>25-mm-filter</i></b>	1.0	2	25

<sup>a</sup> The Aerodynamic Lens Systems Calculator (Wang and McMurtry 2006a, 2006b) was implemented for the aerodynamic lens developed by Liu et al. (1995).

<sup>b</sup> The sample collection time used for the analytical measurement sensitivity calculations was 1 minute.