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Long-Term Measurement of PM_{2.5} Mass Concentration Using an Electrostatic Particle Concentrator-Based Quartz Crystal Microbalance Integrated With Carbon Dioxide Aerosol Jets for PM Sensing in Remote Areas

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ABSTRACT Fine particulate matter (PM_{2.5}) is a major environmental health risk. Several instruments based on the quartz crystal microbalance (QCM) have been developed for PM_{2.5} measurement because of their accurate, sensitive, real-time, and low-cost mass measurements. However, prolonged or non-uniform deposition on the quartz crystal can cause nonlinear responses between frequency shifts and mass deposition, and its frequent manual cleaning with wet sponges is required. These disable long-term measurements of the instruments, thus limiting their applications in remote areas. Herein, we present a new PM_{2.5} instrument called qEPC-Snow. This instrument consists of a QCM crystal embedded in an electrostatic particle concentrator (EPC) for collection and sensing of PM_{2.5} and a carbon dioxide aerosol (snow) jet unit for residue-free, rapid, effective, and non-destructive cleaning of the crystal. Laboratory tests were conducted with aerosolized 100-nm and 2- μ m polystyrene latex microspheres as PM_{2.5} representatives to evaluate (i) frequency responses and (ii) mass sensitiveness of qEPC-Snow, (iii) particle removal efficiencies, and (iv) reuse of the used crystals. Experimental results demonstrated high removal efficiencies (approximately 99.9% for both particle sizes) and statistical similarity between the initial and cleaned QCM crystals in the frequency shift-mass deposition relationship, thereby enabling measurement for more than one month without demounting the crystals. The mass sensitivity was 57.34 (Hz/ μ g) with $R^2 = 0.9904$, corresponding to 0.05667 [(Hz/min)/(μ g/m³)] in mass concentration sensitivity for the PM_{2.5} representatives. The influence of particle sizes on qEPC-Snow's frequency behaviors will also be discussed in detail.

INDEX TERMS Carbon dioxide snow cleaning, electrostatic particle concentrator, PM_{2.5} mass concentration measurement, quartz crystal microbalance, remote sensing.

I. INTRODUCTION

Atmospheric pollution has several detrimental impacts on human health and is a significant concern for the global community [1]. Particulate matter (PM), a major air pollutant, originates from several sources such as traffic, fuel burning, natural dust, and industrial activities [2]. PM with an

aerodynamic diameter of 2.5 μ m or less (PM_{2.5}) has attracted significant attention [3] because these fine particles can easily pass through the filtration of nose hairs and penetrate deeply into the lung [4]. Moreover, PM_{2.5} can carry toxic matter such as viruses and bacteria into a human lung, increasing the prevalence of the respiratory disease [5], [6] and necessitating measuring its concentration level.

Many instruments for PM mass concentration measurement using principles such as radiometric (e.g., beta gauge

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attenuation), gravimetric, optical, and microbalance methods have been presented [7]. Beta gauge attenuation is one of the most extensively used methods for PM mass concentration measurement. It uses a radiometric source to emit beta particles and then measures the degree of their attenuation through a collected mass, where the attenuation is proportional to the collected mass. This method is straightforward and relatively simple [8]. However, its major drawbacks are the use of radioactive sources and the necessity of long-time sampling to obtain sufficient responses [9]. Another common technique involves a gravimetric approach using filters or impactors. The collecting plate is weighed with a precise balance before and after aerosol deposits [10]. Although simple and accurate in measurement [9], gravimetric methods are time-consuming because of long sampling periods for sufficient mass collection and filter weighing steps [11]. PM mass concentration can also be measured with optical instruments, which usually rely on light scattering. These instruments offer high sensitivity [8], ease of use, and low power consumption [12], [13]. However, a primary disadvantage of such methods is that the amount of scattering light depends strongly on diverse particle characteristics such as size, shape, density, and refractive index [8], [9].

Instruments based on the quartz crystal microbalance (QCM) have also been developed for PM_{2.5} mass concentration measurement [14]–[16]. In contrast to optical instruments, QCM can directly measure the mass deposited on its oscillating (electrode) region [17]. These instruments use a QCM crystal as both a collecting spot and a sensing element. PMs can be guided toward the QCM crystal electrode by impaction [14], [16], [18] or by electrical forces [15], [19]. These instruments possess high sensitivity, short sampling periods, low cost, and real-time and accurate measurement [20], [21].

A significant, long-standing weakness of these instruments is that prolonged and/or non-uniform exposures can cause overloading (i.e., the formation of multiple layers of deposited particles) on the crystal electrode [22]. This overloading can cause a breakdown of the linear response between deposited mass and frequency shift because multiple layers of mass deposition can lead to weak bonding with freshly deposited aerosol particles [23]. Thus, it is critical to clean the quartz crystal regularly to ensure long-term, accurate measurements [23], [24].

Several methods are currently used to clean the QCM crystal after aerosol particles are accumulated, such as wiping with a damp cloth [25] or a wet sponge [19]. However, the QCM crystal must be demounted from the body of the instrument and then cleaned and dried manually, hindering long-term or unmanned measurements in remote areas.

Non-liquid-based cleaning techniques have also been explored. Compressed air can be used for surface decontamination. However, this technique is subject to very low removal efficiencies for sub-micrometer and micrometer-sized particles [26]. A carbon dioxide (CO₂) snow jet was proposed to overcome this drawback, with many studies conducted for

its use in the semiconductor industry [27]. This technique relies on mechanical impact and chemical interactions of solid CO₂ (dry ice) particles generated through a nozzle. These dry ice particles are bombarded onto the contaminants along with gaseous nitrogen (N₂) and CO₂, removing deposited sub-micrometer to micrometer-sized particles effectively. This technique showed a residue-free, rapid, effective, and non-destructive cleaning method for a variety of substrates and contaminants [28]–[30].

In this study, we present an electrostatic particle concentrator (EPC)-based QCM (qEPC) integrated with CO₂ aerosol jets for the long-term measurement of PM_{2.5} mass concentration in remote areas, referred to as qEPC-Snow. It is similar to the qEPC we developed previously [15], [31], [32], with a CO₂ aerosol jet unit to enable cleaning the crystal without demounting. One inlet and two outlets were positioned on top of the instrument. A quartz crystal was located on the bottom side, functioning as a collection spot and a sensing element. The top electrode of the crystal was wired to a negative DC voltage potential while all the other walls of qEPC-Snow were electrically biased to the ground. This electrical configuration enhanced the electric field strength over the quartz crystal and concentrated aerosols evenly on the quartz crystal electrode [15], [31], [32], reducing the possibility of overloading. A cleaning unit consisting of CO₂ and N₂ gas nozzles was also located on the side of qEPC-Snow for repetitive crystal cleaning. Several characteristics, such as PM_{2.5} measurements, removing efficiencies, and long-term measurements via the crystal regeneration, will be provided.

II. EXPERIMENTAL METHODS

A. qEPC-SNOW FABRICATION

Fig. 1A illustrates a 3D drawing of qEPC-Snow developed in this study. The instrument was modelled in Solidworks software (Dassault Systèmes Corporation, version 2019). One inlet and two outlet ports, used sequentially for aerosols injection and withdrawing, were located on the top of the instrument. A QCM crystal holder (28 mm in diameter and 23 mm in height) was fixed on the bottom center of the collection chamber. Two arms were fixed on the bottom part and served as a support of the aerosol nozzle package (K6-10DG-A, Applied Surface Technologies, NJ). This nozzle package was positioned at the side of the chamber body, with its injector head through a built-in hollow on the side-wall. This hollow was designed so that its center line (dashed line in Fig. 1A) was set at an angle of 45° to the QCM crystal surface. Fig. 1B illustrates the detailed structure of the QCM crystal holder. A QCM crystal (QCM5140CrAu120-050-Q, Quartz Pro AB, Sweden; diameter: 14 mm) was sandwiched between the cap and the body of the holder. A ring was used to secure the crystal anti-rotationally while screwing the cap via threaded joints. All parts of qEPC-Snow were constructed of aluminum except that the QCM crystal holder (body, cap, and ring) was constructed of ABS plastic. Fig. 1C illustrates an image of the manufactured qEPC-Snow.

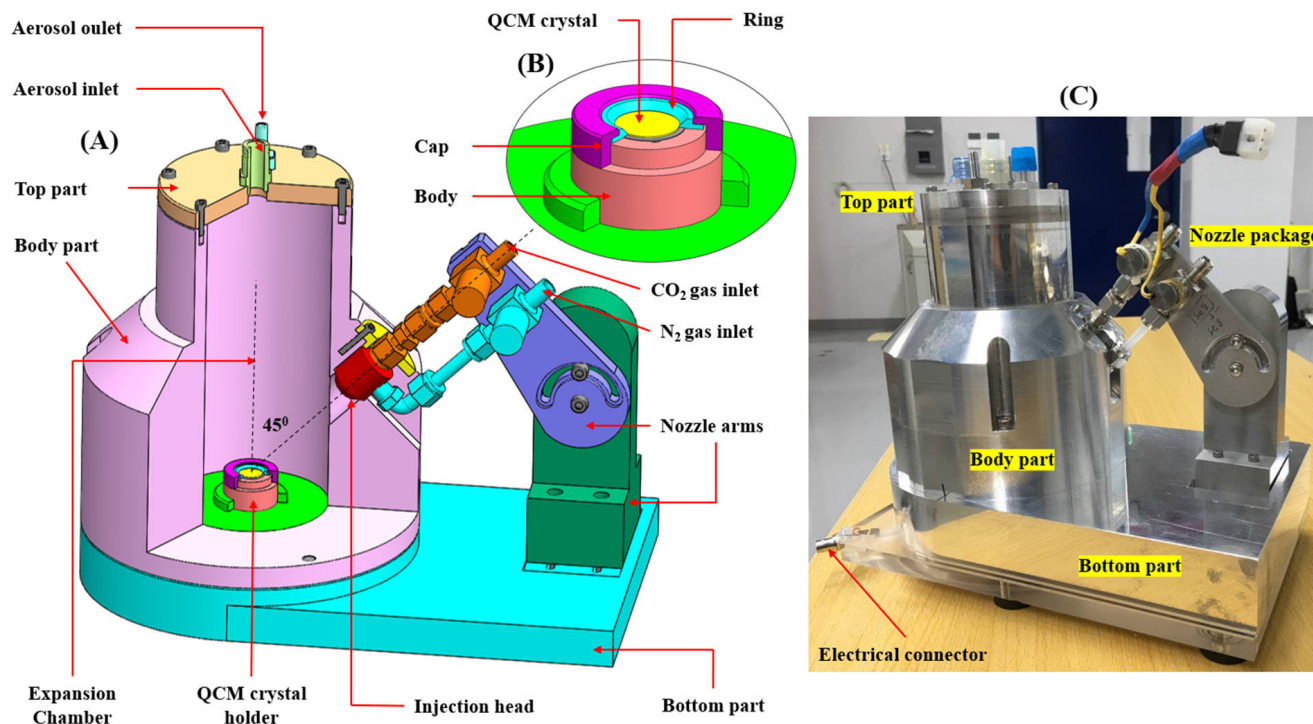


FIGURE 1. Design drawings and an actual image of qEPC-Snow device. (A) A 3D model and major parts of qEPC-Snow. Partial section view illustrates QCM crystal and cleaning injector’s location inside qEPC-Snow. Two dash lines indicate center lines. (B) 3D sub-drawing demonstrates the QCM crystal holder structure and how the QCM crystal is fixed inside qEPC-Snow. (C) Photograph of the fabricated qEPC-Snow.

B. EVALUATION SETUP

The experimental schematic of qEPC-Snow is similar to that of our previous studies [15], [33] (Fig. 2A). Clean and dry compressed air was generated through a clean air supplier unit (Dekati, Finland). The downstream airflow was then divided into two branches. One airflow branch was injected into a three-jet Collision nebulizer (Mesa Laboratories, Denver, CO) at 3 liters per minute (LPM), which contained a diluted suspension of polymer beads (either 100 nm at 0.013wt% or 2.0 μm at 0.02wt%; Thermo Scientific, US) in DI water, for producing monodisperse aerosol particles. These particles were passed through a diffusion dryer (HCT, South Korea) and then a diffusion neutralizer (model 5.622, GRIMM, Germany) equipped with an AM-241 radioactive source to remove water vapors from the aerosolized particles and neutralize the particles, respectively. These neutralized particles were diluted with another clean air stream (10 LPM for 2.0-μm; and 7.5 LPM for 100-nm particles) from the other branch. All airflow rates were precisely controlled using mass flow controllers (model 5850E, Brooks Instrument, PA).

A three-way manifold was used to extract the aerosol particles from the mixing line (line #1). These airborne particles had concentrations of 53.86±8.5 μg/m³ for 100-nm beads and 50.7±9.3 μg/m³ for 2.0-μm beads, and they were moved into a corona charger with a needle wired to a voltage of +3kV (SJ-2000S, Sejin electronics, Korea) and a case grounded for unipolar-charging airborne particles. These charged particles were fed to qEPC-Snow’s inlet port. At the

outlet ports of qEPC-Snow, a scanning mobility particle sizer (SMPS; model 5.416, GRIMM, Germany) or an optical particle sizer (OPC; model 1.109, GRIMM, Germany) was connected to count the actual concentration level of the aerosols for 0.1-μm and 2.0-μm beads, respectively (Fig. 2B). A DC voltage of -10kV (SJ-2000S, Sejin electronics, Korea) was wired to the top electrode of a QCM crystal while the other remaining parts of qEPC-Snow were grounded. Signal acquisition of the QCM crystal was performed by a QCM controller (QCM200, Stanford Research Systems, US).

A dual gas unit consisting of two separate nozzles of CO₂ and N₂ was used to generate CO₂ aerosols. Two high-purity gases (DEOKYANG CO., LTD, South Korea) of CO₂ (99.99%) and N₂ (99.999%) were fed to both control valves for each cycle (Fig. 2C), which helped to adjust the gas streams at desired pressures (5.5 MPa for CO₂ and 0.7 MPa for N₂) and generate dry ice particles (Fig. 2D) [29].

III. METHODS FOR qEPC-SNOW EVALUATION

A. METHODS FOR CALCULATING THE ACCUMULATION OF MASS DEPOSITION AND FREQUENCY SHIFT

The mass deposition on the QCM crystal electrode after each collection period was calculated as follows:

$$m_{deposition}[\mu g] = N \left[\frac{\#}{L} \right] Q \left[\frac{L}{min} \right] t[min] m_p[\mu g] \quad (1)$$

where N is the number concentration, particles/liter (#/L), extracted from OPC or SMPS data, Q is the volume flow

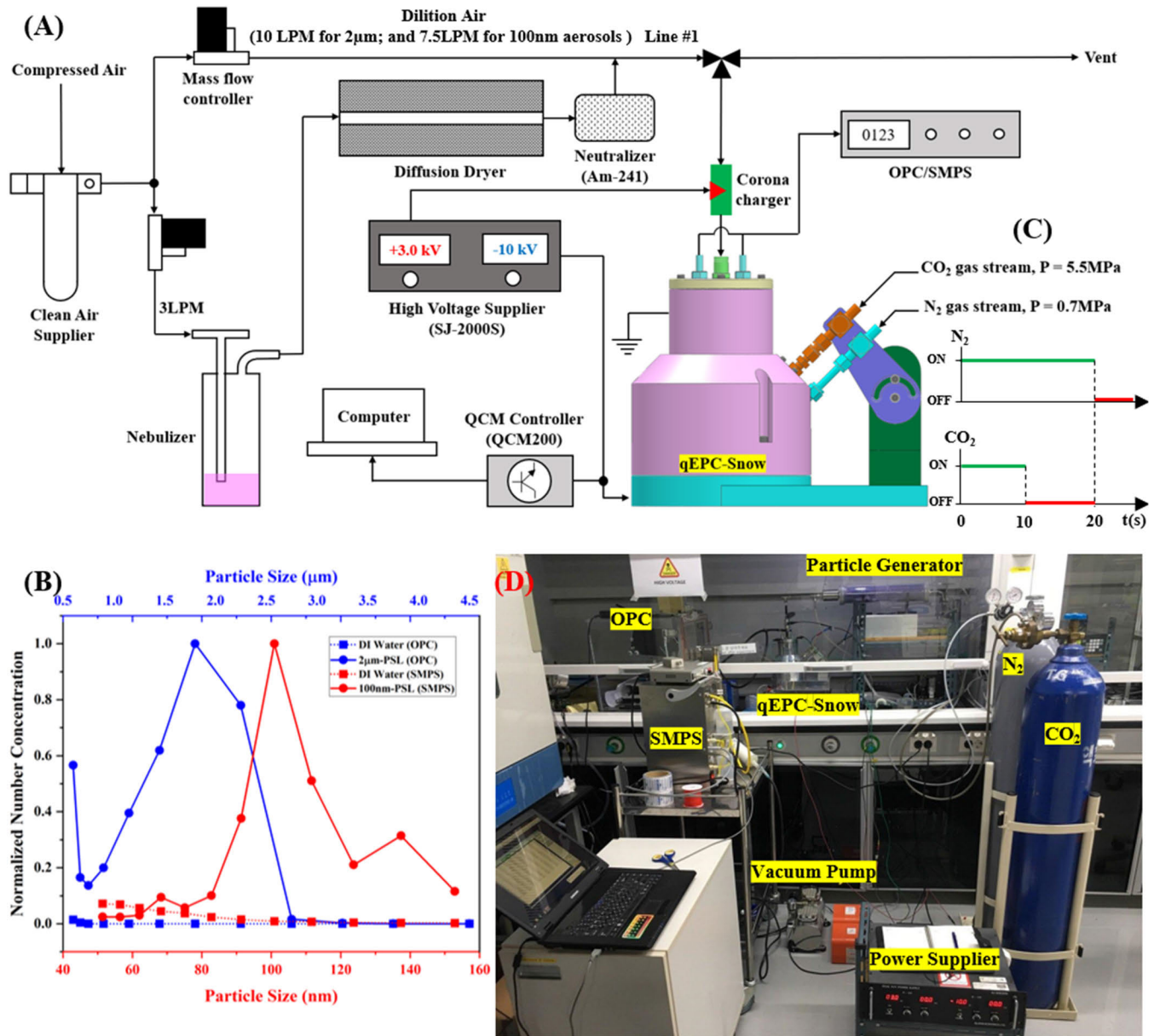


FIGURE 2. Setup for qEPC-Snow device evaluations. (A) Experimental schematic. CO₂ and N₂ cylinders are not depicted. (B) Particle size distributions of DI water alone and 2-µm and 100-nm particles in DI water, measured by OPC (blue) and SMPS (red), respectively. The concentration level of each size was normalized with that of peak size. (C) One aerosol injection cycle. The lime and red colors sequentially indicate the open and close state of each control valve. (D) Photograph of experimental setup.

rate, 1.2 LPM, t is the collection time, equal to 30 minutes in our study, and m_p is the mass of a single polystyrene latex (PSL) particle. Thus, the accumulation of mass deposition and frequency shift can be obtained as follows:

$$m_{accumulation} [\mu g] = \sum m_{previous} [\mu g] + m_{current} [\mu g] \quad (2)$$

$$\Delta F_{accumulation} [Hz] = \sum \Delta F_{previous} [Hz] + \Delta F_{current} [Hz] \quad (3)$$

where m and ΔF sequentially represent the deposited mass and respective frequency shift. The subscripts “accumulation,” “previous,” and “current” denote the accumulated, previous, and current measurement values, respectively.

B. METHODS FOR FREQUENCY SHIFT RESPONSE EVALUATIONS

First, the fabricated qEPC-Snow was connected to the QCM controller to obtain initial frequency signals (F_0) for 10 minutes. The instrument was then disconnected from the controller and connected to the high voltage supply. Next, the generation of the aerosol particles was initiated, and a high voltage (+3kV) was applied to the corona charger for 5 minutes. A collection step was performed by turning on the high voltage (-10kV) for 30 minutes. Afterwards, the -10kV high voltage source was removed, and qEPC-Snow was re-connected to the QCM controller to obtain frequency

signals (F_j) for 10 minutes. The index j indicates each collection step ($j = 1 - 6$) for a total collection time of 180 min. The frequency shifts during each collection interval (30 minutes) were calculated by subtracting the current signals (F_j) from the initial signals (F_0). The accumulation of mass deposition and respective frequency shifts were determined as explained in Section III-A.

C. METHODS FOR CLEANING EFFICIENCY EVALUATIONS

After the 180-min particle deposition, the loaded QCM crystal was demounted from qEPC-Snow. The crystal was positioned under a fluorescence optical microscope (Nikon Eclipse 80i) equipped with a mono-color camera (CoolSNAPTM DYNO, PHOTOMETRICS) to capture images of the initial particle deposition. The crystal was then mounted again into qEPC-Snow and exposed to aerosol jets. The treated crystal was again removed from qEPC-Snow, and images of the crystal electrode were captured. The cleaned QCM crystal was reused ten times. A combination of 10-min initial frequency measurement, a total of 180-min collection with 10-min frequency measurements between each collection period, and subsequent snow cleaning were conducted eleven times.

Three different cleaning procedures were conducted to determine which provided the best cleaning performance. The first involved N₂ (pressure = 0.7 MPa) gas stream alone, and the other two performed CO₂ snow cleanings, which combine both CO₂ (pressure = 5.5 MPa) and N₂ (pressure = 0.7 MPa) gaseous jets, with different injection cycles (1 and 2 cycles). One injection cycle consists of a 10-second duration of CO₂ aerosol during a 20-second duration of N₂ gas (Fig. 2C). For QCM crystals covered with 2- μ m particles, the cleaning efficiency for each of the three removal procedures was calculated as follows:

$$\eta_1 [\%] = 100 \frac{N_1 [\#] - N_2 [\#]}{N_1 [\#]} \quad (4)$$

where N_1 and N_2 are the numbers of total particles (#) counted on the crystal electrode before and after treating with aerosol cleaning jets, respectively. The method for counting particles on the crystal electrode was described in our previous study [15]. ImageJ software (version 1.53e) was used to count the number of particles on the images captured. These data were used to calculate the total number of particles on the entire QCM crystal electrode.

The above particle counting methods were invalid for the crystal covered with 100-nm particles because of multiple-layer formation over the QCM crystal electrodes. Thus, the cleaning efficiencies were estimated as follows:

$$\eta_2 [\%] = 100 \frac{F_c [\text{Hz}] - F_6 [\text{Hz}]}{F_0 [\text{Hz}] - F_6 [\text{Hz}]} \quad (5)$$

where F_c is the fundamental resonance frequencies (Hz) of the QCM crystals cleaned for reuse, F_0 is the frequency (Hz) before mass deposition of the QCM crystals, and F_6 is the frequency (Hz) after 180-min mass deposition of the

QCM crystals, corresponding to $j = 6$ in Section III-B. Furthermore, the efficiency of the snow cleaning was also confirmed by visually examining scanning electron microscope (SEM) micrographs (Cold FE-SEM S4800, Hitachi High-Technologies, Japan) of the crystal electrode before and after snow cleaning.

D. STATISTICAL METHOD FOR QCM CRYSTAL REUSE ESTIMATION

QCM crystals were reused ten times, and the linear fitting with a zero intercept was used to determine its mass sensitivities each time to assess reusability. An analysis of variance (ANOVA) was used to statistically compare the slopes of the QCM crystal between initial use (S_0) and each reuse (S_i with $i = 1, 2, \dots, 10$). The confidence level was set to 95%, and $p > 0.05$ indicates that the compared sets are not statistically different. All data evaluations were performed in Microsoft Excel software using its Data Analysis add-in.

E. METHODS FOR DETERMINING qEPC-SNOW'S MASS CONCENTRATION SENSITIVITY

The mass sensitivities (S_m) were determined by linear fit analyses with a zero intercept for all measurement points. The mass concentration sensitivity (S_{conc}) can be computed from the mass sensitivity (S_m) value as follows:

$$S_{conc} \left[\frac{\text{Hz}/\text{min}}{\mu\text{g}/\text{m}^3} \right] = S_m \left[\frac{\text{Hz}}{\mu\text{g}} \right] Q \left[\frac{\text{L}}{\text{min}} \right] 10^{-3} \left[\frac{\text{m}^3}{\text{L}} \right] \quad (6)$$

IV. RESULTS AND DISCUSSION

This section presents the frequency measurements, cleaning efficiencies, QCM crystal reusability, linear response ranges, and sensitivities of qEPC-Snow. The measurement of frequency shifts due to added mass is a primary consideration of any QCM-based instrument. Removals of deposited particles from the crystal electrodes are of great interest for reusing the crystal because they significantly affect the long-term measurement of qEPC-Snow. The mass sensitivity [$\text{Hz}/\mu\text{g}$] was experimentally obtained with two representatives of PM_{2.5} (100-nm and 2- μ m diameter particles) and compared with the value predicted by the Sauerbrey equation because commercial PM_{2.5} instruments measure a particle size range of 0.1 – 2.5 μ m. Eventually, the mass concentration sensitivity [$(\text{Hz}/\text{min})/(\mu\text{g}/\text{m}^3)$] calculated by (6) was presented and compared with another QCM based sensor.

A. FREQUENCY MEASUREMENTS

A shift in a QCM crystal's resonant frequency is linearly proportional to the mass deposited on it, referred to as the Sauerbrey behavior [34]. This linearity is valid only when the mass is firmly attached to the crystal electrode in the form of rigid films [35]. Unfortunately, the shear motion of the QCM crystal and the absence of electrical force during the frequency measurements might rupture or loosen the mass-to-electrode contacts [35], especially in the

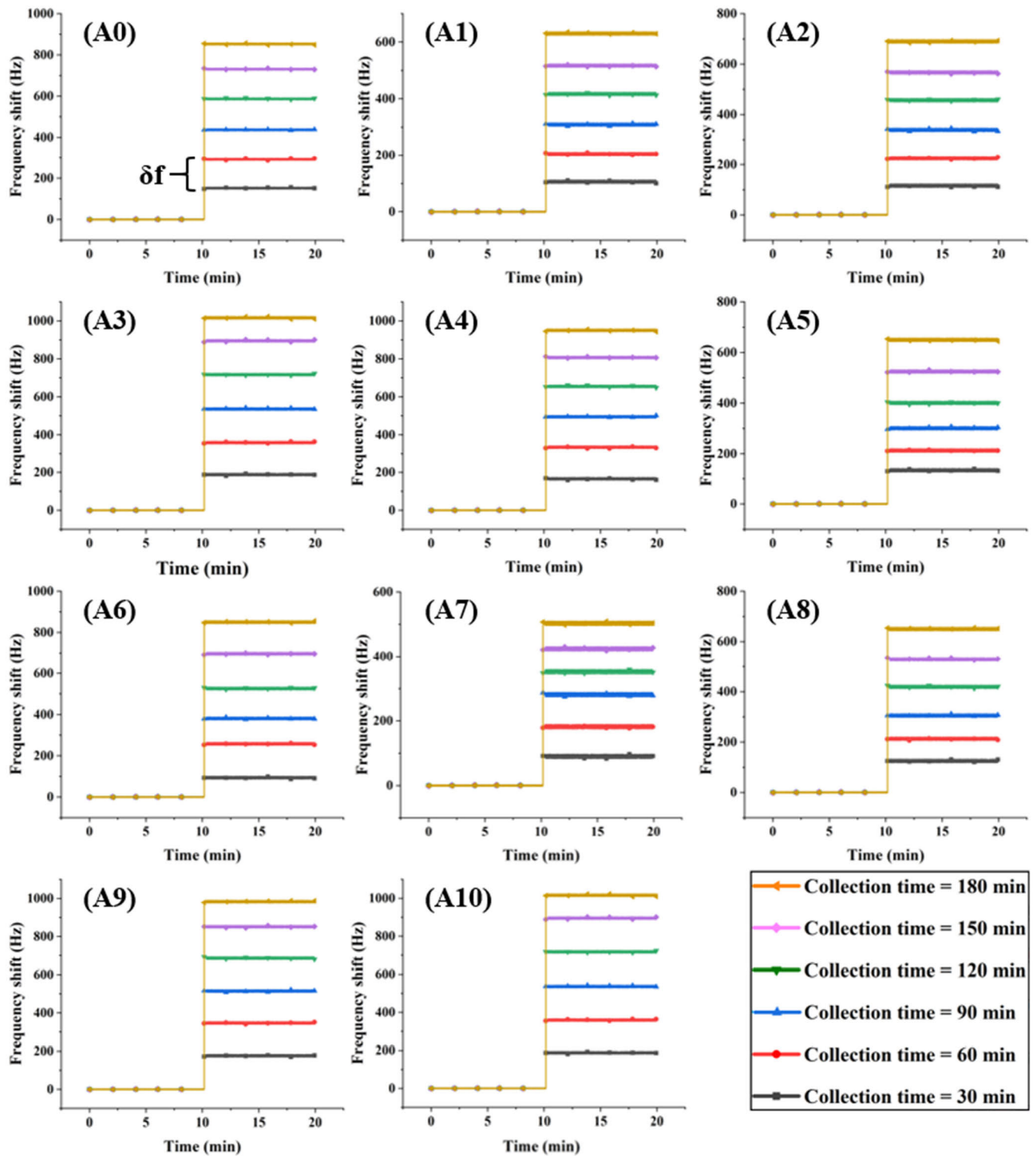


FIGURE 3. Frequency shift measurements of qEPC-Snow for the 2- μm -diameter particles under various QCM crystal conditions. A0 represents the responses of the initially used QCM crystal. A1 to A10 represent crystal's responses after different (1st–10th) cleaning stages. Symbol δf denotes shifts in resonant frequencies after each collection interval (30 minutes).

case of multiple-layer formation. This can cause nonlinear frequency-mass relationships [34], [36].

The frequency shifts of the initial (Fig. A0) and reused QCMs (Fig. A1 to Fig. A10) were measured with various collection periods for 2- μm aerosolized particles (Fig. 3).

The measured signals were nearly constant, with a standard deviation (S.D.) of 0.5 Hz, during 10 min at all collection periods. The shifts in resonance frequencies after each collection interval (30 min), denoted by δf , were almost equal with an S.D. of 9.5 Hz. These two imply sufficient

attachments of 2- μm particles on the QCM electrodes, leading to the linear behavior even at high mass deposition (18 μg) corresponding to 180-min collections. The frequency shifts relative to the initial frequency measurements at the same collection periods of A0–A10 were not identical, which may be due to the inconsistency in the concentration of the generated aerosols and/or residual particles not detached completely from the crystals by the aerosol cleaning. The particle concentration of the initial suspension is not invariant with time when the particles in the suspension are nebulized [37].

The same behaviors were also observed for the QCM crystal tested with 100-nm particles when the collection periods were 120 min and shorter. For longer periods, the δf tended to decrease as the collection time increased (Fig. 4). Given the high collection efficiency ($\sim 99\%$), the reductions suggest that fresh 100-nm particles were deposited to form multiple layers on the crystal electrode. These newly formed layers were loosely bound to the inner layers, thus not effectively sensed by the crystal and causing the nonlinear behavior. The frequency measured for the collection periods longer than 120 min remained nearly constant (S.D. = 0.48 Hz). This result reveals that the outer particles to inner layer contacts occurred instantly during the collection periods and the contacts were so weak that many of fresh particles did not fully attach to the sensor crystal surface, not contributing to any positive shift in the resonance frequency, and only a few fresh particles attached to the sensor crystal surface. These observations were essential for further evaluations of qEPC-Snow because any disturbance in frequency shifts might produce nonlinear responses leading to inaccurate measurements of qEPC-Snow.

B. CLEANING AND RECYCLING OF THE QCM CRYSTALS

Fluorescence and SEM images of the QCM crystal electrode were taken before and after treatments with various cleaning strategies (Fig. 5). Low cleaning efficiencies were observed for the N_2 gas flow cleaning, whereas high cleaning efficiencies were observed with the CO_2 snow cleanings for both particle sizes tested. Fundamentally, the adhered particles can be removed when the removal forces exceed the adhesion forces exerted on the particles by the surface [38], in which the adhesion forces are proportional to the particle diameter. The aerodynamic drag force exerted on adhered particles by gas flow is proportional to particle diameter squared [39]. Moreover, a rapid decrease in the velocity in the boundary layer causes an immediate reduction in the drag force required to dislodge the particles [26]. Consequently, the N_2 gas stream could not sufficiently detach the deposited particles from the crystal electrode, resulting in low cleaning efficiencies of approximately 10.52% for the 2- μm particles.

In contrast, the snow cleaning removed adhered particles by momentum transfer from cryogenic dry ice particles to the adhered particles, dislodging them from the crystal electrode [26]. The dislodged particles were then easily carried away by the gas flow over the surface. In this study, the use

of this cleaning method confirmed high cleaning efficiencies, approximately 99.99% for the 2- μm particles and 99.98% for 100-nm particles even with only one cycle, corresponding to 20 seconds. This cleaning period is much lower than those of commercial instruments, such as Kanomax Piezobalance Dust Monitor 3522, Respirable Aerosol Mass Monitor 3511, and Respirable Aerosol Mass Monitor 8511, requiring at least 2 min to clean and dry the QCM crystal manually [40]–[42]. Furthermore, although the cleaning efficiencies were over 99.9%, several of attached particles remained on the surfaces (Fig. 5) with and without being noticed by the measurements, which caused slight differences in the initial reference frequencies between each stage.

The frequency shifts of qEPC-Snow were measured as functions of accumulated mass for two sizes of particles, 100 nm (Fig. 6A) and 2 μm (Fig. 6B), during the initial and ten reuse stages of the QCM crystal using the snow cleaning. In each stage, 10-min initial frequency measurement, six 30-min collections with six 10-min frequency measurements, and subsequent snow cleaning were conducted. The mass sensitivities measured between the cleaned and the initial crystals did not differ significantly ($p > 0.057$ for 2- μm particles and $p > 0.091$ for 100-nm particles) (Table 1) based on the 95% confidence intervals. This means that the crystals were free of mechanical damage such as crystal deformation or breaks due to the impingement of the jets. The generated dry ice particles, a sublimable substance, had a range of 0.4 to 9.6 μm with a peak of 0.7 μm , and the mechanical impact on the substrate was minimal [43].

These crystals were used for collection periods up to 1,980 minutes through ten-fold reuse. Given that the PM measurement can be performed each per hour for 3–5 min [15], these total collection periods correspond to 16.5–27.5 days without demounting the crystals. The total collection periods can be extended to more than a month by the additional aerosol cleaning without any residues of CO_2 aerosols, demonstrating that our proposed system can be used for long-term monitoring in remote areas. In contrast, frequent wet cleaning (e.g., every 40 min or so with a wet sponge) is required for a commercial dust monitor [40].

C. LINEAR RESPONSE RANGES AND MASS SENSITIVITIES

Figure 6A and 6B illustrate the linear response ranges of qEPC-Snow for both sizes of the particles. qEPC-Snow exhibited linear responses up to 9.2 μg ($R^2 = 0.9926$) and 18 μg ($R^2 = 0.9952$) of mass loadings for 100-nm and 2- μm particles, respectively. The variation in the mass sensitivity after each cleaning was measured, and the average mass sensitivity and relative standard deviation (RSD) were 57.8 [Hz/ μg] and 4.2%, respectively (Fig. 6C). Hence, qEPC-Snow can ensure reasonable measurements of recycled QCM crystals.

The difference between the two linear response limits was investigated by visually examining the particle deposition structures on the crystal electrodes. The closed views of these structures taken by SEM images (Fig. 6D) revealed

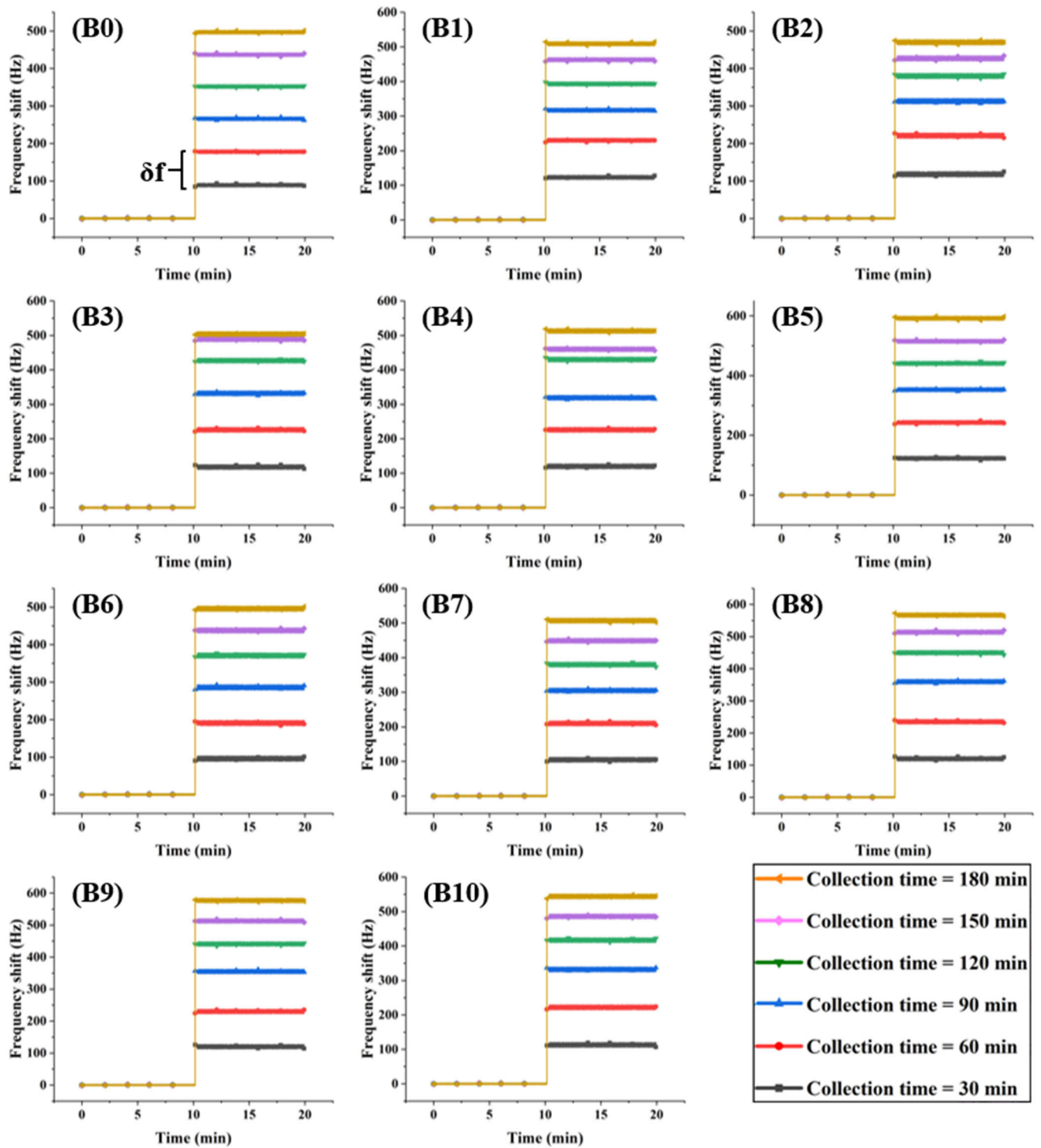


FIGURE 4. Frequency shift measurements of qEPC-Snow for 100-nm diameter particles under various QCM crystal conditions. B0 represents responses of initially used QCM crystal. B1 to B10 represent crystal’s responses after different (1st–10th) cleaning stages. Symbol δf denotes shifts in resonant frequencies after each collection interval (30 minutes).

that the 2- μm particles were deposited as a single layer even at approximately 18 μg , or the nonlinearity threshold. The corresponding number of particles was 4.05×10^6 , and the corresponding number of layers was 0.17 when we compared the total projected areas of all the particles with the

crystal electrode area. This result indicates that most particles deposited directly stuck to the crystal electrode without forming even a single layer. Moreover, high and non-uniform electrical fields generated in qEPC-Snow [15], [31] might strengthen the particle–electrode contacts more firmly. These

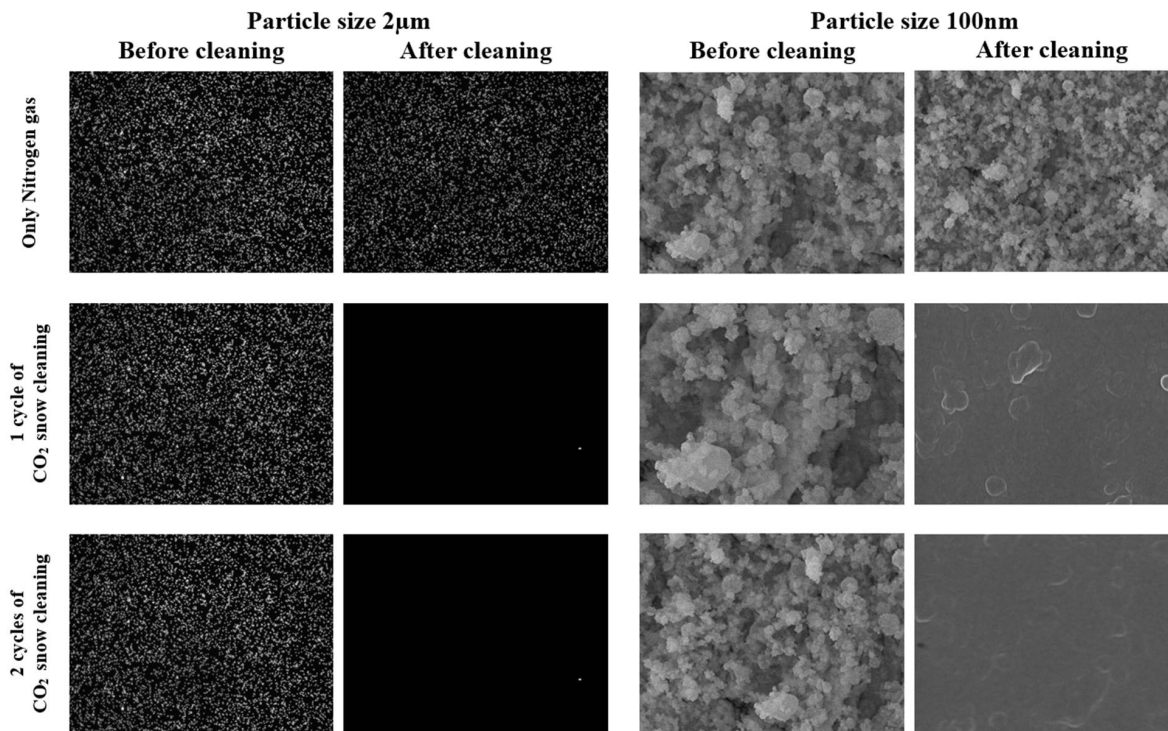


FIGURE 5. Fluorescence optical images (20X) of 2-µm and high-magnification (30000X) of SEM images of 100-nm particle sizes on QCM crystal electrodes under various cleaning conditions.

TABLE 1. p-values of the analysis of variance (ANOVA) tests of mass sensitivities (Hz/µg) relative to non-reused and initial crystal.

n-th cleaning step	Particle size	
	2 µm	100 nm
1	0.0571	0.2551
2	0.0589	0.0919
3	0.3957	0.1611
4	0.8320	0.3446
5	0.1081	0.5450
6	0.7900	0.5455
7	0.8211	0.2084
8	0.0717	0.3557
9	0.5348	0.1241
10	0.1482	0.1241

two may lead to the linear response of the QCM crystal even at large mass loadings.

Similarly, the deposition of the 100-nm particles exhibited a single layer below the threshold of linear response, 9.2 µg,

as visualized in Fig. 6E. The corresponding number of 100-nm particles was 1.66×10^{10} , and the corresponding number of layers was 1.74. The results revealed single particles plus their agglomerates (252 ± 57 nm in size) on the

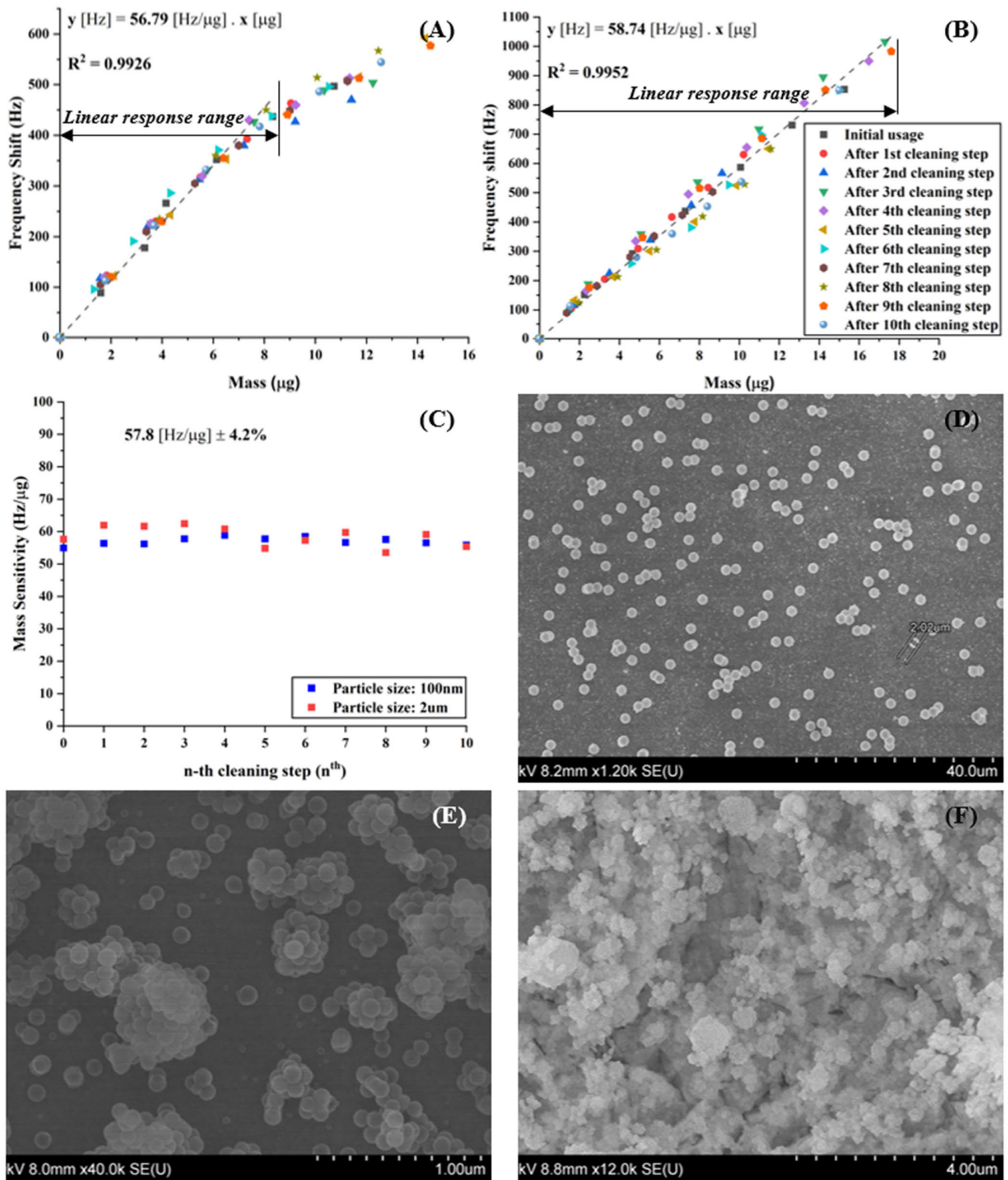


FIGURE 6. (A) and (B) illustrate frequency shift of qEPC-Snow evaluated with 100-nm and 2- μm particles, respectively. Dashed lines represent linear fits of all points and legend in (B) is for both graphs. Frequency shift and mass are accumulated values calculated by the methods in Section III-A. (C) indicates variances of the mass sensitivity after each cleaning stage. High-magnification SEM images of: (D) the 2- μm particles at 18 μg deposition; (E) 100-nm particles at 8.6 μg ; and (F) 100-nm particles at 11.2 μg of mass deposition. Images were shot at the center of the QCM crystal electrode.

crystal surface, with the most severe aggregation for small polymer particles ($\sim 100\text{ nm}$) [44]. In contrast, multiple layers and particle agglomerations on the crystal electrode were

significant above the linear response limit (e.g., 11.2 μg), as in Fig. 6F. In such a structure, fresh particles cannot firmly adhere to the crystals' electrode. These agglomerations

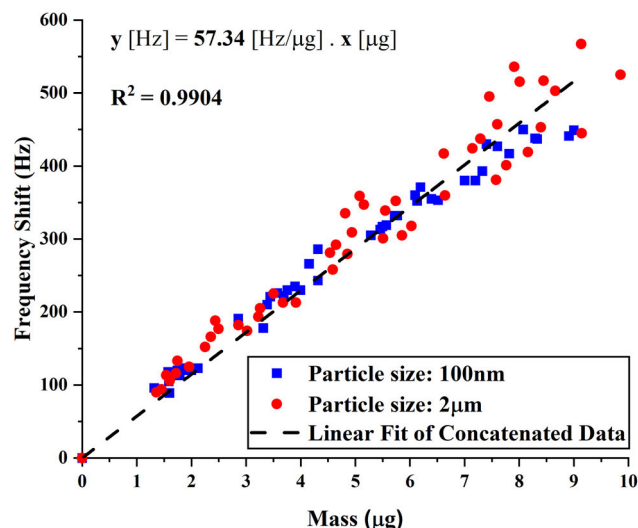


FIGURE 7. Overall experimental mass sensitivity of qEPC-Snow. Theoretical mass sensitivity predicted by the Sauerbrey equation was 50 Hz/ μg for the 5 MHz QCM crystal used in this study. Frequency shift and mass are accumulated values calculated by the methods in section III-A.

cannot be effectively sensed, so the linearity between the frequency shift and mass change was not maintained.

The measured mass sensitivities were 56.79 (Hz/ μg) with $R^2 = 0.9926$ for 100-nm particles (Fig. 6A) and 58.74 (Hz/ μg) with $R^2 = 0.9952$ for 2- μm particles (Fig. 6B). The inequality between the two sensitivities results from differences in particle size, affecting how much the particles gain electrical charges and agglomerate, hence the deposition structure on a crystal. A zero intercept linear fit of all datasets in the linear response ranges of qEPC-Snow exhibited a mass sensitivity of 57.34 (Hz/ μg) with $R^2 = 0.9904$ (Fig. 7). This sensitivity is greater than the theoretical value, 50 (Hz/ μg), predicted by the Sauerbrey equation. The reasons for this discrepancy are that the Sauerbrey equation assumes that the properties of the added mass such as density, shear modulus, and acoustic impedance are identical to those of quartz [17], [45], and the added mass is a completely rigid, infinitesimal, and uniform film, which is not the case for the aerosol particle capture in this study [23], [46].

Finally, qEPC-Snow aims to measure the PM_{2.5} mass concentration in practice. The mass concentration sensitivity was calculated based on (6) as 0.05667 [(Hz/min)/($\mu\text{g}/\text{m}^3$)]. This value is slightly greater than that obtained from another QCM-based PM sensor using impaction, 0.05540 [(Hz/min)/($\mu\text{g}/\text{m}^3$)] [21]. This difference was made because qEPC-Snow had higher collection efficiencies and a more even distribution of aerosol deposits on the QCM crystal electrodes [15].

V. CONCLUSION

In this study, we present a novel PM_{2.5} instrument called qEPC-Snow for long-term measurements of PM_{2.5} mass concentration and experimental evaluations obtained by exposing

the instrument to two PM_{2.5} representatives, 100-nm and 2- μm PSL. The instrument consists of an EPC to collect charged aerosols evenly onto an embedded QCM crystal and a dual gas unit located on the EPC's side for particle removal. The laboratory tests confirmed that (i) qEPC-Snow's frequency response was linear up to 9.2 μg of all PM_{2.5} representatives deposition, resulting in 57.34 (Hz/ μg) with $R^2 = 0.9904$ for mass sensitivity or 0.05667 [(Hz/min)/($\mu\text{g}/\text{m}^3$)] for mass concentration sensitivity, (ii) the collected aerosols can be effectively removed from the QCM crystal, over 99.9% for both sizes, thus making the crystal available for reuse ten times, and (iii) in comparison with several commercial PM measurement instruments, qEPC-Snow exhibits outstanding performance, such as longer aerosol collection time while retaining the linear behavior of the QCM, and a much shorter period required to clean the crystal; drying is not needed because of sublimation of dry ice particles upon their contacts on the crystal surface (supplementary video). Given these features, qEPC-Snow can measure PM_{2.5} for more than a month without demounting the crystals for their cleaning. Therefore, the demonstrated platform can be potentially applied to air quality monitoring in remote areas.

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