An Investigation of Factors Affecting Measurement Accuracy of Nanoparticles Real-time Sensor using Corona Discharge integrated with Quartz Crystal Microbalance

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\textbf{Abstract.} A nanoparticles real-time sensor in the present study was designed using corona discharge integrated with quartz crystal microbalance (QCM) or Nano-QCM detector. We investigated the following factors affecting the measurement accuracy of the detector; needle to plate distance, flow rate, and number of particles on QCM. DC high voltage power supply of 7 kV was used to maintain the positive corona voltages difference in the charger. The mass sensitivity of 10 MHz AT-cut QCMs coated by plate rigid gold film were investigated. The monodisperse aerosol particles smaller than 300 nm were initially used for the testing of the system. They were charged with negative corona voltages and then deposited on the surface of QCM electrode. Sauerbrey equation was used to describe the frequency-mass relationship at the QCM surface. Results show that the above factors significantly affect the accuracy of the detector measurement. The particles can be collected on a QCM electrode using the partial breakdown high voltage (reach to breakdown points) in terms of needle-to-plate corona discharge. The optimal needle-to-plate distance is 6 mm with maximum mass change (frequency shift) on QCM electrode of 0.607μg/min. The QCM collection efficiency of nanoparticles on the QCM electrode surface using corona discharge technique can be as high as 95% of total particles. Collection efficiency of PM\textsubscript{0.1} is under investigation.
1. Introduction

Air pollution is one of significant problems in Thailand. The problem impact on many sides in the society including economy, transportation and, especially health and environment. Development of new technics and knowledge is necessary for real time measurement and monitoring of air quality. United State Environmental Protection Agency (USEPA) defines the national ambient air quality standards (NAAQS) and classifies the particle in term of particulate matter (PM) in 2 sizes including course particle (PM$_{10}$) and fine particle (PM$_{2.5}$) (EPA, 2018). Recently, the classification of the particulate matter is also including the ultrafine particle or PM$_{0.1}$ or nanoparticles. Although the nanoparticles are not widely concerned and defined in air quality criteria, they are harmful and have greater impact to human than PM$_{10}$ and PM$_{2.5}$ (Herder, et al.,1986; Oberdorster, et al., 2004; Jaques & Kim, 2000; Chen, et al., 2016).

The particle mass concentration measurement devices were improved from several techniques used for example (1) Electrical Low Pressure Impactor (ELPI) - particles are discharged in a corona charger and classified by impactor and are detected by high sensitive aerosol electrometer (Järvinen, Aitomaa, Rostedt, Keskinen, & Ojanperä, 2014). (2) Electrical Aerosol Detector (EAD) - particles are discharged by unipolar diffusion charger. The charged particles are detected by high sensitivity aerosol electrometer (Li, Chen, & Tsai, 2009). (3) Real-Time QCM-MOUDI Impactor - application of Micro-Orifice Uniform Deposition Impactor (MOUDI) and real-time mass detection based on Quartz Crystal Microbalances (QCM) sensors (Chen, Romay, Li, & Naqwi , 2016). (4) Nanosampler or PM0.1 sampler - cascade impactor which operate on the principle of inertial impaction (Furuuchi, et al., 2010). (5) Personal nanosampler or PM0.1 personal sampler – to use inertial filter (IF) which cut off particle size by the principle of inertial impaction (Thongyen, et al., 2015). (6) Monitoring system consisted of electrostatic PM mass monitor (PM$_{10}$ and PM$_{2.5}$ particles) – particles are classified by impactor and discharged in a corona charger and then are measured electrically by PM detector (Intra, et al., 2019a; 2019b; 2020; 2021). For the particle mass concentration measurement device, real-time measurement techniques have been recently developed and gained more acceptance (Li, Chen, & Tsai, 2009; Järvinen, Aitomaa, Rostedt, Keskinen, & Ojanperä, 2014; Thongyen, et al., 2015; Chen, Romay, Li, & Naqwi, 2016). However, a low cost and online particulate monitoring system for measuring the mass concentrations of ambient PM$_{0.1}$ is limited, especially Quartz Crystal Microbalance (QCM) technique. Therefore, the unipolar needle-plate corona charger technique integrated with QCM for real time nanoparticle (PM$_{0.1}$) mass concentration measurement should be developed and field tested

In the present study, the investigator is interested to use the unipolar needle-plate corona charger technique integrated with Quartz Crystal Microbalance (QCM) for real time nanoparticle (PM$_{0.1}$) mass concentration measurement or Nano-QCM Detector. Personal nanosampler combined with inertial filter which has been developed by researchers from Kanazawa University (Furuuchi, et al., 2010; Otani, Eryu, Furuuchi, Tajima, & Tekasakul, 2007) was used to classify the particle size before passing through the corona charger and measured by QCM. The unipolar needle-plate corona charger is the most common technique to produce high ion concentrations. This technique is mostly used in discharge particle field due to high charging efficiency and simple structure (Alonso, Martin, & Alguacil, 2006; Choi & Kim, 2007; Qi, Chen, & Greenberg, 2008; Intra P., 2012). The charged particles move and deposit on QCM following the principle of electrostatic. QCM could measure highly sensitive mass balance up to nanogram to microgram level changes by frequency oscillation. When addition mass is deposited on the QCM surface, the frequency shift occurs. The difference of frequency can determine in mass per unit area (Sauerbrey, 1959) for real time monitoring.

2. Theoretical and principle

2.1 The corona discharge of needle to plate

The DC steady corona current and voltage relationship for point-to-plane geometry is given by (Townsend, 1914)

$$I = AV(V - V_0)$$  \hspace{1cm} (1)
where \( I \) is the corona discharge current (A), \( V \) is the applied voltage (V), \( V_0 \) is the corona onset voltage (V) and \( A \) is the dimensional constant depending on the inter-electrode distance, the needle electrode radius, the charge carrier mobility in the drift region and other geometrical factors.

The mathematical model for microscopic point-to-plane coronas in the steady-state regime was developed for prediction of the relationship between corona current and voltage in gaseous media depending on the distance between the needle tip and the plane by (Henson, 1981).

\[
I = \frac{2\pi kF}{\alpha} \left( \frac{\delta}{\alpha} \right)^{1/2} (V - V_0)^{3/2}
\]

(2)

where \( \delta \) is the minimum corona glow radius (m), \( \alpha \) is the distance between the needle tip and the plane (m), \( \varepsilon \) is permittivity \((\text{C}^2/\text{N.m}^2)\) \( K \) is a dimensional constant and \( F \) is a polynomial function of \( \frac{\delta}{\alpha} \).

The critical electric field strength, \( E_c \) (V/m), for corona onset prediction is given by the Peeks's equation. The equation considers the effects of temperature and pressure, but the effect of air humidity was not included.

\[
E_c = m_\nu E_0 \delta \left( 1 + \frac{k}{\sqrt{\delta r}} \right)
\]

(3)

where

\[
\delta = \frac{P}{P_r} \frac{273 + T}{273 + T_r}
\]

(4)

\( m_\nu \) is the roughness coefficient of surface of conductor (1 for smooth cylindrical electrodes), \( r \) is the radius of curvature of the needle tip (m), \( E_0 \) is the electric field strength onset (V/m), \( k \) is the empirical constant for cylindrical geometry (normally 0.308 cm^{1/2}), \( \delta \) is the relative air density factor (kg/m³), \( T_r \) is the absolute temperature of room air (K), \( P_r \) is the normal atmosphere pressure (bar), and \( T \) and \( P \) are the operating temperature (K) and pressure of the air (bar). For Peek's equation, the standard reference atmospheric condition is adopted, i.e. \( P_r=101.3 \text{ kPa} \) and \( T_r=20^\circ \text{C} \). At normal temperature and pressure conditions, the corona onset voltage, \( V_0 \), can be approximated by

\[
V_0 = m_\nu E_0 \delta \left( 1 + \frac{k}{\sqrt{\delta r}} \right) r \ln \left( \frac{S}{r} \right)
\]

(5)

where \( S \) is the distance between the needle electrode and nozzle (m). The air relative humidity is not used to estimate in this equation.

The modified equation which includes the air relative humidity around conductor is determined by (Yawootti et al, 2015)

\[
V_0 = m_\nu E_0 \delta \left( 1 + \frac{k}{\sqrt{\delta r}} \right) r \ln \left( \frac{S}{r} \right) \left[ 1 + \left( 5.76 - \frac{1.63}{0.69 \sqrt{\delta r} + 0.21} \right) \right] \cdot \frac{P_w}{P_r} \cdot H
\]

(6)

and

\[
P_w = 611 \times 10^{7.5T/(237.3+T)}
\]

(7)

where \( H \) is the air humidity, \( P_w \) is the partial pressure of saturated water vapor (bar).

The QCM collection efficiency of nanoparticles on the QCM electrode surface was calculated by

\[
\text{Collection efficiency} = \left( 1 - \frac{N_{\text{out}}}{N_{\text{in}}} \right) \times 100
\]

(8)

where \( N_{\text{in}} \) is particle number concentration of inlet QCM prototype (particle/L). \( N_{\text{out}} \) is particle number concentration of outlet QCM prototype (particle/L) which are measured by optical particle counter (OPC).
2.2 Quartz Crystal Microbalance (QCM)

Sauerbrey (1959) discovered the relationship between mass absorption on the surface of quartz and offset of its frequency in gas phase. When the particles deposit on the electrode surface, the frequency decreases from the fundamental resonance frequency. The frequency shift ($\Delta f$) can be defined by Sauerbrey's equation:

$$\Delta f = -\frac{2f_0^2}{\sqrt{\rho_q\mu_q}} \frac{\Delta m}{A}$$

where $\Delta f$ is the measured resonant frequency change (Hz), $f_0$ is the intrinsic frequency of the quartz crystal (Hz) which depends primarily on plate thickness and cut crystal face, $A$ is the active crystal area or electrodes area (cm$^2$), $\rho_q$ is the density of quartz (2.643 g/cm$^3$), $\mu_q$ is the shear modulus of quartz for the AT-cut crystal ($2.947 \times 10^{11}$ g/cm s$^2$), and $\Delta m$ is the mass changing (g).

3. Experimental Setup

![Experimental setup for QCM Prototype.](image)

The experimental setup for investigating the optimum value of flow rate and distance between tip to plate of QCM prototype is shown in Figure 1. The 300 nm monodisperse polystyrene latex (PSL) particles generated by an atomizer flow through a diffusion dryer. The outlet relative humidity is between 45-50%. The particles were charged by 7 kV corona discharge and induced to the QCM electrode. The frequency shift was monitored by a frequency counter and oscillator circuit. The data were transferred to the data acquisition circuit by using Bluetooth communication. Particle concentration was measured by an optical particle counters (OPC) in term of particle number concentration.
Figure 2. shows the configuration of QCM prototype. The variation of the distance from tip to plate represents variation of electric field strength which affects the charging efficiency of QCM prototype. The distance was varied from 6-20 mm. Air flow rate inlet was 4.67 lpm. The frequency shift was reported from the data acquisition device. The inlet aerosol flow rate was varied from 1.25 - 3 lpm by using the flow meter.

4. Results and Discussion

4.1 The relationship between distance from tip to plate and frequency shift.

The relation between distance from tip to plate and frequency shift is shown in Figure 3. The frequency shift represents the particle concentration which is induced on electrode. Frequency shift is inversely proportional to the distance from tip to plate. At the distance below 6 mm, breakdown occurs. Therefore, the distance of 6 mm is the optimal value for this condition. The sensitivity of the QCM when 300 nm particles were used is represented by the shift when the high voltage supply was turned off and it is shown in Figure 3. It decreases from 0-100 in 60 s.
4.2 The relationship between aerosol flow rate and frequency shift.

![Figure 4](image-url)

**Figure 4** The relationship between aerosol flow rate and frequency shift from 1.25-3 lpm.

![Figure 5](image-url)

**Figure 5** The comparison affecting of frequency shift between on and off high voltage for 2 and 3 lpm air flow rate.

The relation between aerosol flow rate and frequency shift is shown in Figure 4. The highest frequency shift occurs at 1.25 and 1.5 lpm. The higher air flow rate will lead the high concentration of aerosol in the charging zone (between tip to plate) and the aerosol was charged with less efficiency. The suitable values of the flow rate are between 1.25-1.5 lpm. Figure 5 shows the comparison affecting of frequency shift when the high voltage was turned on and off for the flow rate of 2 and 3 lpm. The result is obviously different between 2 and 3 lpm when on and off high voltage. Thus, the air flow rate has a large effect to the induction of aerosol on the QCM electrode.

Moreover, the conversion of frequency shift to particle number concentration and QCM collection efficiency of 6 mm distances were calculated by Eq (9) and Eq (8), respectively. Results shows that the mass change or particle number concentration on QCM electrode is 0.607 μg/min. The collection efficiency of QCM integrated with the unipolar needle-plate corona charger technique was found to be 95% of total particles for 300 nm particles. This is consistent with the study of real-time detection of particles by using electrical detection of charged particles (Intra, et al., 2019a; 2019b; 2020; 2021).
5. Conclusion

The distance from tip to plate and the aerosol air flow affect the induction of particles on a QCM electrode. In this configuration of QCM prototype, optimal needle-to-plate distance is 6 mm with maximum mass change (frequency shift) on QCM electrode of 0.607 μg/min. The QCM collection efficiency of nanoparticles on the QCM electrode surface using corona discharge technique can be as high as 95% of total particles.

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