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Technical Note

Filterable and Condensable Fine Particulate Emissions from Stationary Sources

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ABSTRACT

$PM_{2.5}$ emissions from stationary sources contain a filterable and condensable portion. In this study, USEPA Method 201A/202 are used to measure filterable and condensable $PM_{2.5}$ emissions from 5 stationary sources (power plants, boilers, brick manufacturing plant, incinerators and arc furnaces). The average filterable $PM_{2.5}$ concentrations for power plant, boiler, brick manufacturing plant, incinerator and arc furnace are 0.75, 16.9, 8.67, 0.15 and 2.12 mg/Nm^3, respectively. The amount of $PM_{2.5}$ residue on the exit tube of cyclone and front half of the filter holder is significantly higher when the filterable $PM_{2.5}$ concentrations are low. It is necessary to collect both filter and the residue particulates to avoid underestimation of $PM_{2.5}$ emissions. The condensable PM accounts for 61.2%, 73.5%, 44.2%, 52.8% and 51.2% of total $PM_{2.5}$ for power plant, boiler, brick manufacturing plant, incinerator and arc furnace plant, respectively. The real $PM_{2.5}$ contribution to the atmosphere would be underestimated if condensable PM is not included. The condensable PM fraction increases as the exhaust temperature rises. The inorganic fraction accounts for 89.0%, 69.4%, 72.3%, 89.8% and 72.8% of condensable PM, respectively, for power plant, boiler, brick manufacturing plant, incinerator and arc furnace. The inorganic fraction is dominant in the condensable PM, which might be due to the high content of SO_4.

Keywords: Fine particulate; Stationary sources; Filterable $PM_{2.5}$; Condensable $PM_{2.5}$; Dry impinger method.

INTRODUCTION

Previous studies have shown that fine particulate (aerodynamic size less than 2.5 μm, $PM_{2.5}$) is harmful to human health (e.g., Pope *et al.*, 2004; Chang *et al.*, 2012). The level of atmospheric $PM_{2.5}$ is associated with cardiovascular disease and mortality (Pope *et al.*, 2004; Chiu *et al.*, 2013). It is essential to reduce $PM_{2.5}$ emission and control its formation in order to lower the level of atmospheric $PM_{2.5}$. To realize the $PM_{2.5}$ characteristics and estimate the contributions from the emission sources is the first step of emission control.

The main sources of atmospheric $PM_{2.5}$ include volcanic eruption, sea salt spray, street dust, direct discharge of industrial processes and transport emissions (Chow *et al.*, 1995; Gugamsetty *et al.*, 2012; Subramoney *et al.*, 2013). The combustion stationary sources are important $PM_{2.5}$ contributors (Sudheer and Rengarajan, 2012; Ward *et al.*, 2012; Yu *et al.*, 2013). Particulate matter emissions from stationary sources contain filterable and condensable portion. Filterable PM are particles directly emitted from a stack as a solid or liquid at stack conditions and captured on the filter of a sampling train. Condensable PM means material that is vapor phase at stack conditions, but condenses and/or reacts upon cooling and dilution in the ambient air to form solid or liquid PM immediately after discharge from the stack. Condensable PM is typically not measured because most countries do not require sources to measure it. $PM_{2.5}$ emission would be underestimated if condensable $PM_{2.5}$ is not included since condensable PM accounts for a significant portion for $PM_{2.5}$. USEPA has announced Method 201A and Method 202 to measure filterable PM and Condensable PM, respectively. Numerous studies have investigated the measurement artifacts of Method 202. The measurement artifacts have been reduced by optimization of the new method (Corio and Sherwell, 2000; Richards *et al.*, 2005).

In addition to USEPA Method 201A/202, various types of dilution systems for the measurement of $PM_{2.5}$ have been developed (e.g., Kong *et al.*, 2013; Lee *et al.*, 2013). Dilution sampling system collects filterable PM and condensable PM on the same filter and the chemical compositions can be analyzed. However, a few parameters would affect the measurement accuracy of the dilution sampling system and the standard specification is still developing. Before the standard or the guidelines of the dilution methods are established, USEPA Method 201A and 202 are the standard method for $PM_{2.5}$ measurement of stationary sources. Moreover, the extremely large bulky sampling equipments

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make it difficult to measure $PM_{2.5}$ emissions for many important sources. At this stage, USEPA Method 201A/202 is the most practical way to collect $PM_{2.5}$ samples from the stationary sources. Since CPM is seldom measured, very few literatures for condensable PM emission characteristics have been reported in the literature. In this study, USEPA Method 201A/202 are used to measure $PM_{2.5}$ emissions from 5 stationary sources (power plants, boilers, brick manufacturing plant, incinerators and arc furnaces). The emission characteristics of the filterable PM and condensable PM for these important $PM_{2.5}$ emission sources are discussed.

EXPERIMENTAL SECTION

Sampling Campaign

Filterable and condensable $PM_{2.5}$ emitted from 5 stationary sources (power plants, boilers, brick manufacturing plants, incinerators and arc furnaces) were collected in this study. Power plants use coal and oil as fuels. The electricity capacities are 240–550 MW. Electrostatic precipitators are installed to remove PM emissions for all the power plants. Flue gas desulfurization is additionally used to remove SOx emissions for the coal-fired power plants. Boilers use coal as fuel. Most of these boilers are the textile industry. Cyclone and bag house are installed to remove PM emissions for the boilers. Brick manufacturing plants produce tile and brick. The main process is raw material (such as clay or slurries) drying and firing. Incinerators have capacities from 450–900 ton waste combustion per day. Bag houses are installed to remove PM emissions for all the incinerators. Semi-dryer absorption system is used to remove SO_x emissions. Arc furnaces use scrap steel as feedstock. Bag houses are installed to remove PM emissions for all the arc furnaces. At leat 3 successful samples were collected for the 5 stationary emission sources.

Sampling Equipment and Methods

USEPA Method 201A (Determination of PM_{10} and $PM_{2.5}$ emissions from stationary sources) and Method 202 (Dry impinger method for determining condensable particulate emissions from stationary sources) (USEPA, 2010) were performed for filterable and condensable PM measurements, respectively. APEX XC-5000 Automated Isokinetic Sampling Console sampling system which meet the requirement of USEPA Method 201A and Method 202 was used in this study. The main equipment of Method 201A includes front nozzle, $PM_{2.5}$ cyclone, filter holder, pitot tube and stainless steel (with glass liner) sampling tube, vacuum pump and the computer control console. The sampling rate is controlled within ± 20% isokinetically for the sampling in this study. Particulates with diameter less than 2.5 μm are sucked through the cyclone and are primarily collected on a 4.7 mm filter. The temperature of cyclone sampling head is maintained within ± 10°C of the stack temperature to ensure proper sizing and prevent condensation on the walls of the cyclones.

The equipment of Method 202 includes a condenser, water dropout impinger, modified Greenburg Smith impinger and condensable PM filter (Fig. 1). Condensable PM is mainly collected in the water dropout impinger and the (backup) modified Greenburg Smith impinger. Condensable PM filter placed between the second and the third impingers is used to improve the collection efficiency. Condensable PM is collected by condenser, dry impingers, pipelines and the backup Teflon filter after filterable PM is removed by a 4.7 mm filter. In addition, exhaust gas composition (N_2, O_2,

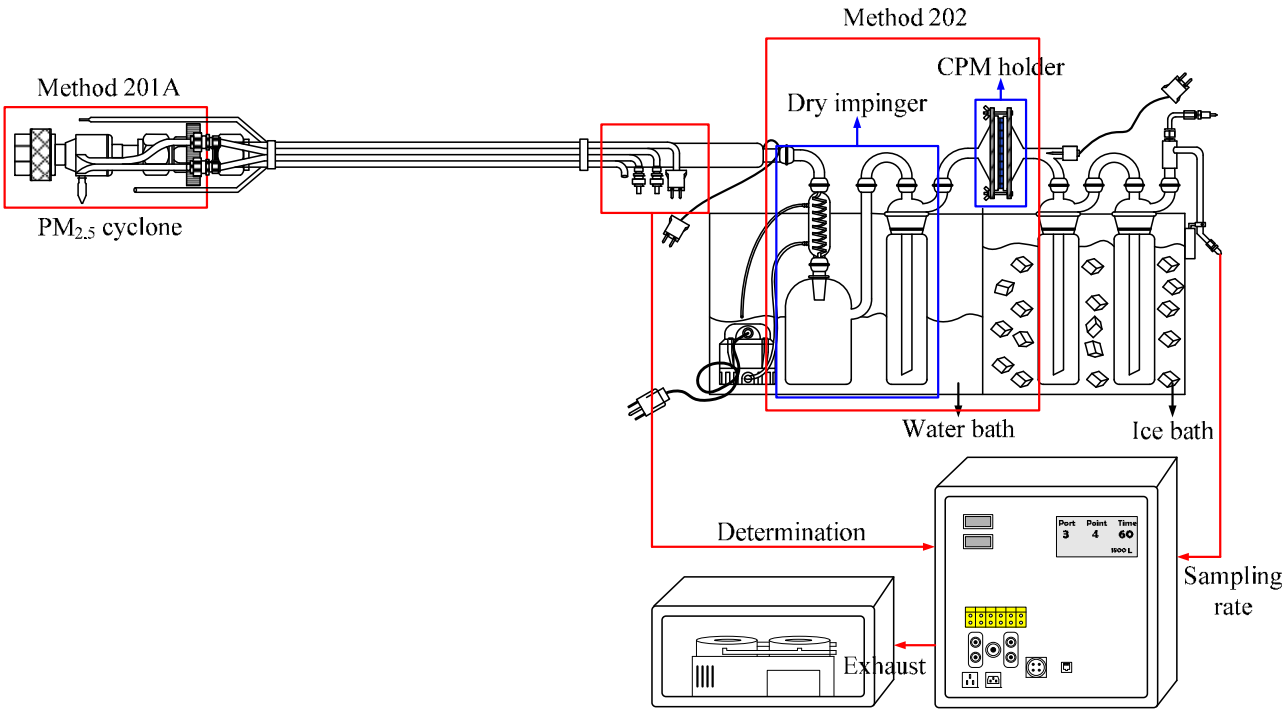

Fig. 1. USEPA Method 201A and Method 202 sampling train.

CO_2, CO) is measured by Orsat method. Leakage check is conducted before each sampling. To collect sufficient sample, the sampling volume is at least than 2 m^3.

Sample Analysis

Filterable $PM_{2.5}$

Pallflex 47 mm quartz filter is used for filterable PM collection. The filter is conditioned under temperature of 20–23°C and relative humidity of 30–40% for 24 hrs before and after sampling. After condition, the filter is weighed by the gravimetric technique (Sartorius balance, model Cubis 6.6S-DF). In addition to the filter sample, $PM_{2.5}$ on the exit tube of cyclone and front half of the filter holder is collected by acetone rinses. The rinses is quantitatively transferred to a tared 250 mL beaker, and evaporated to dryness at room temperature and pressure in a laboratory hood. Desiccate the sample for 24 hrs and weighed (USEPA, 2010).

Condensable $PM_{2.5}$

USEPA Method 202 is used to sample and analyze condensable PM. According to USEPA Method 202, it is necessary to measure condensable PM if the gas filtration temperature exceeds 30°C. Condensable PM is collected in the water dropout impinger, the modified Greenburg Smith impinger and the condensable PM filter of the sampling train. The impinger contents are purged with Ultra-High Purity compressed nitrogen immediately after sample collection to remove dissolved sulfur dioxide gases from the impinger. Condensable PM train is purged at a minimum of 14 L/min for at least 1 hr. Purified water and organic solvents (n-hexane and acetone) were used to rinse the whole sampling pipeline, condenser, water dropout impinger, modified Greenburg Smith impinger and condensable PM filter, respectively. The inorganic (water rinses) and organic (organic solvent rinses) fractions were dried and weighed in the laboratory. Condensable PM is the summation of the two fractions. Field blanks (e.g., Organic solvents and water field blanks) are measured for each sampling. Detailed procedures could be referred to USEPA Method 202.

RESULTS AND DISCUSSION

Filterable $PM_{2.5}$ Concentrations and Its Composition

Filterable $PM_{2.5}$ emission concentrations for the investigated plants are shown in Fig. 2. The average filterable $PM_{2.5}$ concentrations for power plant, boiler, brick manufacturing plant, incinerator and arc furnace are 0.75, 16.9, 8.67, 0.15 and 2.12 mg/Nm^3, respectively. Boilers have highest average emission concentrations.

A filter with 4.7 mm is installed after the $PM_{2.5}$ cyclone to collect the particulate less than 2.5 μm. However, residue might be left on the exit tube of cyclone and front half of the filter holder. According to USEPA Method 201A, the residue should be collected and be combined with the filter data for the emission estimate. The residue was recovered by acetone washing, evaporated, conditioned and weighed. The mass distributions for $PM_{2.5}$ are shown in Fig. 3. Most $PM_{2.5}$ was collected on filter, and only about 5% $PM_{2.5}$ was retained at the cyclone holder. For incinerator, significant amount $PM_{2.5}$ is retained at the cyclone holder. The reason is that filterable PM emission concentrations low. Less filterable $PM_{2.5}$ is collected on the filter and the particulate residue left on the exit tube of cyclone and front half of the filter holder is similar for all the plants, which results in the high percentage of the residue mass. The air pollution control devices can reduce PM (as well as $PM_{2.5}$) emissions effectively. $PM_{2.5}$ emissions would be even lower when the devices are used. The results show that it is important and necessary to collect both filter and cyclone holder residue particulates to avoid underestimation of $PM_{2.5}$ emission, especially for the stacks with low $PM_{2.5}$ concentrations.

Condensable $PM_{2.5}$ Concentrations and Its Composition

USEPA Method 202 was used to measure the emission of condensable PM in this study. Condensable PM is collected by condenser, dry impinger and backup filter as shown in Fig. 1. The emission concentrations of condensable PM are shown in Fig. 4. The average condensable $PM_{2.5}$ concentrations for power plant, boiler, brick manufacturing

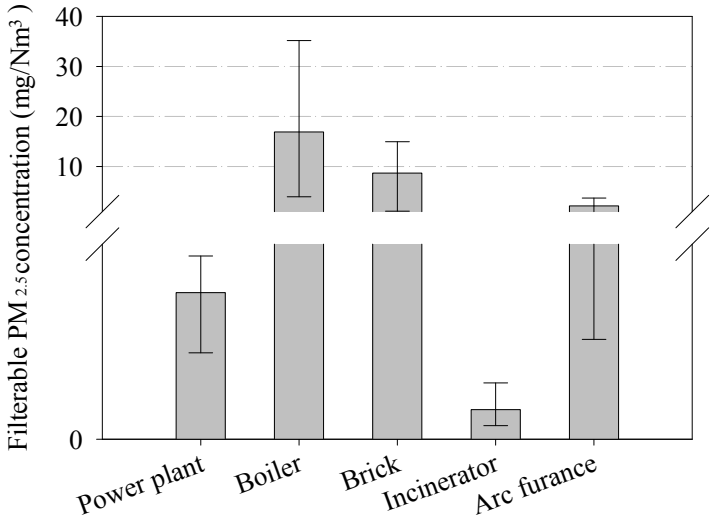

Fig. 2. Filterable $PM_{2.5}$ concentrations for the plants.

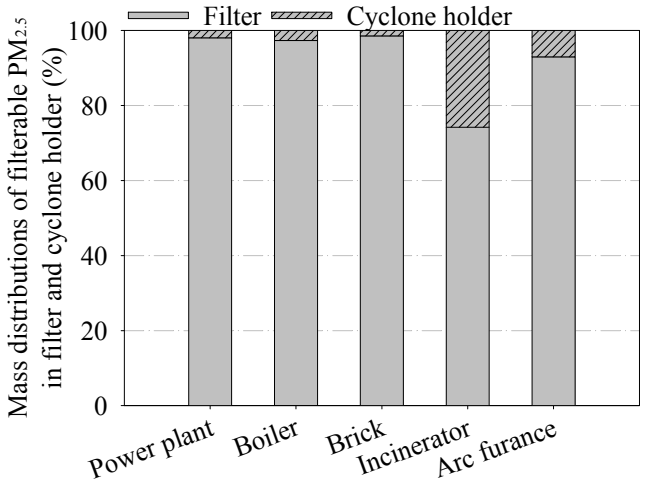

Fig. 3. Average mass distributions of filterable $PM_{2.5}$ on filter and cyclone holder.

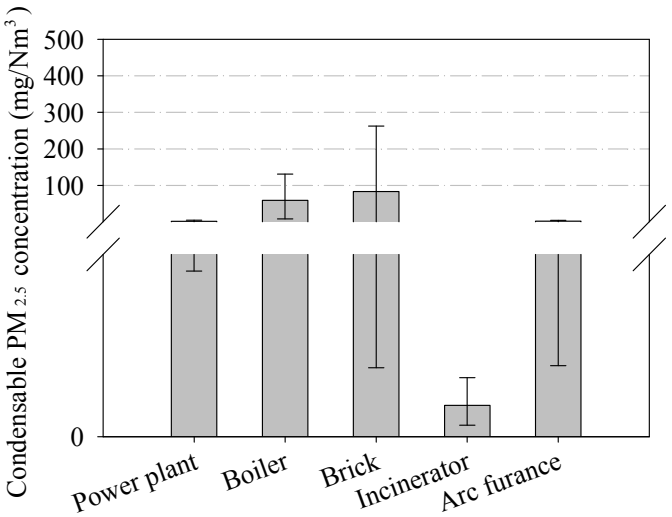

Fig. 4. Condensable $PM_{2.5}$ concentrations for the plants.

plant, incinerator and arc furnace are 2.15, 29.3, 83.5, 0.17 and 2.53 mg/Nm^3, respectively. The same as filterable PM, incinerator has the lowest emission concentrations.

Condensable PM sample is the rinses of the sampling media by water and organic solvents (acetone and hexane) sequentially. Condensable PM thus consists of inorganic fraction (water rinse) and organic fraction (solvent rinse). The partitions of inorganic and organic fraction of condensable PM for the investigated plants are shown in Fig. 5. The inorganic fraction accounts for 89.0%, 69.4%, 72.3%, 89.8% and 72.8%, respectively, for power plant, boiler, brick manufacturing plant, incinerator and arc furnace. Inorganic fraction is dominated in condensable PM. The results agree with the previous studies (Corio and Sherwell, 2000; Richards *et al.*, 2005).

Evaluations of Method 202 for coal-fired boiler emissions showed that the inorganic fraction accounted for higher than 95% of the condensable PM (DeWees *et al.*, 1989). SO_4 compounds, primarily H_2SO_4, make up the largest category of inorganic condensable emissions. During combustion of fossil fuels, sulfur in fuel is oxidized primarily to SO_2 and a small fraction is converted to SO_3. SO_3 reacts with water to form H_2SO_4 in the stack gas. Besides, SO_4 may form if the plants use selective catalytic reduction which add ammonia (NH_3) to control NO_x emission. H_2SO_4 mist and particulate SO_4 may be emitted along with the particulate passing through the control device (Corio and Sherwell, 2000). The high content of SO_4 explains the predominance of inorganic fraction in condensable PM.

Percentages of Filterable and Condensable PM in $PM_{2.5}$

The percentages of filterable and condensable PM in $PM_{2.5}$ for the investigated plants are shown in Fig. 6. Condensable PM dominates for most plants. The condensable PM fraction accounts for 61.2%, 73.5%, 44.2%, 52.8% and 51.2% for power plant, boiler, brick manufacturing plant, incinerator and arc furnace plant, respectively. The results of Corio and Sherwell (2000) show that condensable PM, on average, comprises 76% of the total PM_{10} stack emissions for coal-burning boilers. PM emissions were measured for

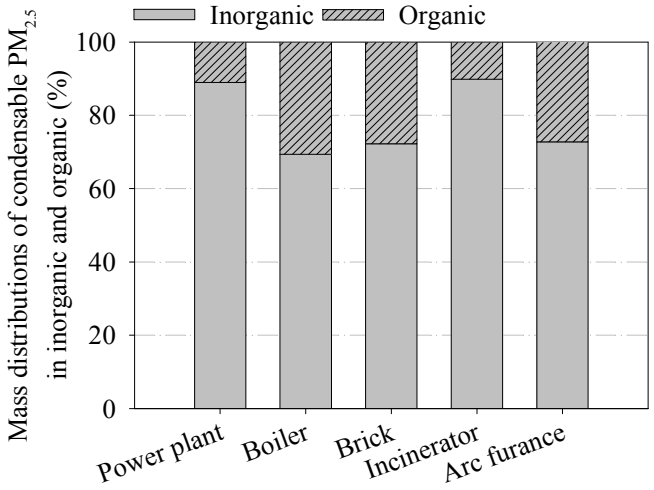

Fig. 5. Distributions of condensable $PM_{2.5}$ in inorganic and organic fractions.

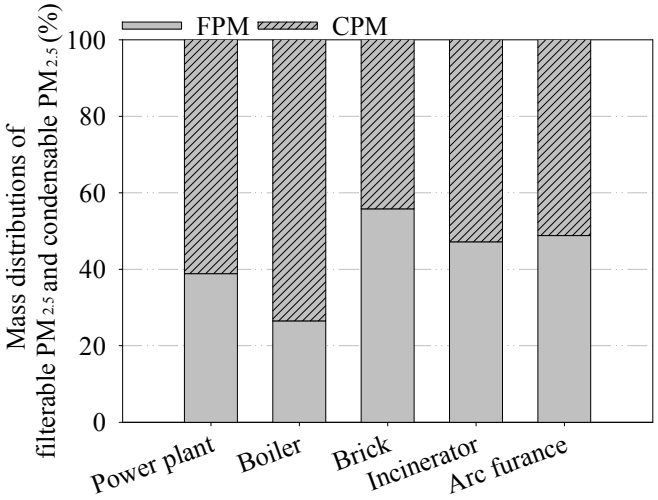

Fig. 6. Mass distributions of $FPM_{2.5}$ and $CPM_{2.5}$ for the plants.

power plants with three different fuels (bituminous, sub-bituminous coal and lignite). The results showed that condensable PM accounts for 59.7%, 49.1% and 73% of total PM emissions for fuels of bituminous, sub-bituminous coal and lignite, respectively (Farber and Sloat, 2005). The results of this study agree with the previous studies. Condensable PM concentrations are higher than filterable PM. This is partially due to better control of filterable particulate combined with emission controls for NO_x that use catalysts that produce SO_3 or use ammonia injection. Condensable PM is not measured typically because regulations in most countries do not require sources to measure. However, the real $PM_{2.5}$ contribution to the atmosphere would be underestimated if condensable PM is not included.

The percentages of condensable PM in $PM_{2.5}$ for different sources vary greatly. Condensable PM percentage depends on control devices, exhaust temperature and other source-specific conditions. Among the factors, stack temperature is the most significant since in-stack filter is used with Method 201A. As shown in Fig. 7, condensable PM percentage increases as the exhaust temperature increases. As mentioned in previous section, when the stack temperature is cooler, the SO_4 and other condensable materials are easier to condense on the filter, which would result in the higher percentage of filterable PM. The results again indicate the importance of including condensable PM in $PM_{2.5}$ emission measurement since stack temperature can affect filterable PM measurement result for in-stack measurement of Method 201A. No matter how the condensable and filterable PM distributions are affected by the stack temperatures, the emission of $PM_{2.5}$ to the atmosphere should be sum of filterable and condensable PM.

CONCLUSION

USEPA Method 201A and 202 are used to measure filterable and condensable $PM_{2.5}$ emissions, respectively, from 5 stationary sources. The average filterable $PM_{2.5}$ concentrations for power plant, boiler, brick manufacturing plant, incinerator and arc furnace are 0.75, 16.9, 8.67, 0.15

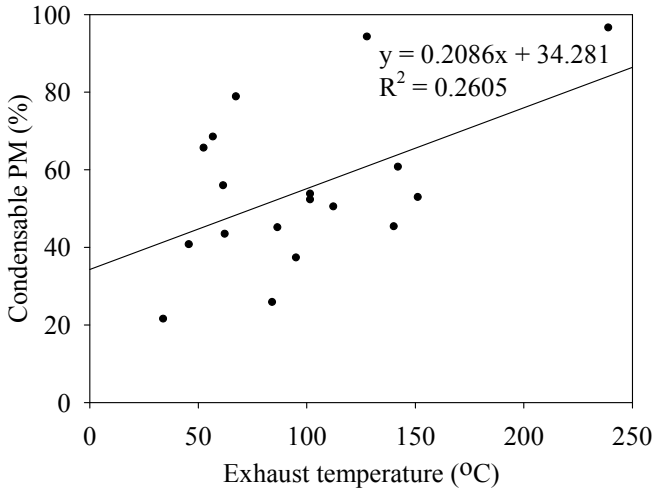

Fig. 7. Correlation between condensable PM percentage and temperature.

and 2.12 mg/Nm^3, and the average condensable $PM_{2.5}$ concentrations are 2.15, 29.3, 83.5, 0.17 and 2.53 mg/Nm^3, respectively. For filterable $PM_{2.5}$ collection, it is necessary to collect both filter and the residue particulates to avoid underestimation of $PM_{2.5}$ emission since the amount of $PM_{2.5}$ residue on the exit tube of cyclone and front half of the filter holder is significantly high when filterable $PM_{2.5}$ concentrations are low. The inorganic fraction accounts for 89.0%, 69.4%, 72.3%, 89.8% and 72.8% of condensable PM, respectively, for power plant, boiler, brick manufacturing plant, incinerator and arc furnace. The condensable PM accounts for 61.2%, 73.5%, 44.2%, 52.8% and 51.2% of total $PM_{2.5}$ for power plant, boiler, brick manufacturing plant, incinerator and arc furnace plant, respectively. The real $PM_{2.5}$ contribution to the atmosphere would be underestimated if condensable PM is not included. Stack temperature is an important factor affecting the distribution of filterable and condensable $PM_{2.5}$.

REFERENCES

Chang, C.J., Yang, H.H., Chang, C.A. and Tsai, H.Y. (2012). Relationship between Air Pollution and Outpatient Visits for Nonspecific Conjunctivitis. *Invest. Ophthalmol. Visual Sci.* 53: 429–433.

Chiu, H.F., Peng, C.Y., Wu, T.N. and Yang, C.Y. (2013). Short-Term Effects of Fine Particulate Air Pollution on Ischemic Heart Disease Hospitalizations in Taipei: A Case-crossover Study. *Aerosol Air Qual. Res.* 13: 1563–1569.

Chow, J.C., Fairley, D., Watson J.G., DeMandel, R., Fujita, E.M., Lowenthal, D.H., Lu, Z., Frazier, C.A., Long, G., Cordova, J., (1995). Source Apportionment of Wintertime PM_{10} at San Jose, Calif. *J. Environ. Eng.* 121: 378–387.

Corio, L.A. and Sherwell, J. (2000). In-Stack Condensable Particulate Matter Measurements and Issues. *J. Air Waste Manage. Assoc.* 50: 207–218.

DeWees, W.G., Steinsberger, S.C., Plummer, G.M., Lay, L.T., McAlister, G.D. and Shigehara, R.T. (1989). Laboratory and Field Evaluation of the EPA Method 5 Impinger Catch for Measuring Condensable Matter from Stationary Sources; U.S. Environmental Protection Agency, Research Triangle Park, NC, 1989.

Farber, P.S. and Sloat D.G. (2005). Reducing Acid Mist Emissions from Coal-fired Power Plants, COAL-GEN Power Generation Conference, 2005.

Gugamsetty, B., Wei, H., Liu, C.N., Awasthi, A., Hsu, S.C., Tsai, C.J., Roam, G.D., Wu, Y.C. and Chen, C.F (2012). Source Characterization and Apportionment of PM_{10}, $PM_{2.5}$ and $PM_{0.1}$ by Using Positive Matrix Factorization. *Aerosol Air Qual. Res.* 12: 476–491.

Kong, S.F., Ji, Y.Q., Li, Z.Y., Lu, B. and Bai, Z.P. (2013). Emission and Profile Characteristic of Polycyclic Aromatic Hydrocarbons in $PM_{2.5}$ and PM_{10} from Stationary Sources Based on Dilution Sampling. *Atmos. Environ.* 77: 155–165.

Lee, S.W., Herage, T., Dureau, R. and Young, B. (2013). Measurement of $PM_{2.5}$ and Ultra-Fine Particulate Emissions from Coal-Fired Utility Boilers. *Fuel* 108: 60–66.

Pope, III, C.A., Burnett, R.T., Thurston, G.D., Thun, M.J., Calle, E.E., Krewski, D. and Godleski, J.J. (2004). Cardiovascular Mortality and Long-term Exposure to Particulate Air Pollution: Epidemiological Evidence of General Pathophysiological Pathways of Disease. *Circulation* 109: 71–77.

Richards, J., Holder, T. and Goshaw, D. (2005). Optimized Method 202 Sampling Train to Minimize the Biases Associated with Method 202 Measurement of Condensable Particulate Matter Emissions, 2005 Hazardous Waste Combustion Specialty Conference, St. Louis, Missouri, 2005, Air & Waste Management Association.

Subramoney, P., Karnae, S., Farooqui, Z., John, K. and Gupta, A.K. (2013). Identification of $PM_{2.5}$ Sources Affecting a Semi-Arid Coastal Region Using a Chemical Mass Balance Model. *Aerosol Air Qual. Res.* 13: 60–70.

Sudheer, A.K. and Rengarajan, R. (2012). Atmospheric Mineral Dust and Trace Metals over Urban Environment in Western India during Winter. *Aerosol Air Qual. Res.* 12: 923–933.

USEPA (2010). USEPA Method 201A, Determination of PM_{10} and $PM_{2.5}$ Emissions from Stationary Sources.

USEPA (2010). USEPA Method 202, Dry Impinger Method for Determining Condensable Particulate Emissions from Stationary Sources.

Ward, T., Trost, B., Conner, J., Flanagan, J. and Jayanty, R.K.M. (2012). Source Apportionment of $PM_{2.5}$ in a Subarctic Airshed-Fairbanks, Alaska. *Aerosol Air Qual. Res.* 12: 536–543.

Yu, L.D., Wang, G.F., Zhang, R.J., Zhang, L.M., Song, Y., Wu, B.B., Li, X.F., An, K. and Chu, J.H. (2013). Characterization and Source Apportionment of $PM_{2.5}$ in an Urban Environment in Beijing. *Aerosol Air Qual. Res.* 13: 574–583.

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