SIZE AND CHEMICAL CHARACTERISTICS OF FINE PARTICULATE EMISSIONS FROM OIL AND COAL-FIRED PILOT SCALE BOILERS

S. Win Lee, Ian He, Ted Herage and Bart Young

CANMET Energy Technology Centre
Natural Resources Canada
Ottawa. Canada. K1A 1M2

Introduction

The Canada Wide Standards for particulate matter (PM) was proposed in Canada in 2000, soon after the publication of the new US National Ambient Air Quality Standards in 1997 [1,2]. Subsequently, increased research activities were noted in the following years in addressing the apparent knowledge gaps related to fine PM emissions. Measuring $PM_{2.5}$ and PM_{10} emissions from combustion sources began to replace the traditional means of monitoring and reporting of total suspended particulates. Identification and quantification of PM from regional point sources are critical in controlling the PM emissions effectively at source as well as in apportioning the ambient PM concentrations to the contributing local sources. A new methodology was developed to determine fine PM emissions under plume-simulating conditions that are comparable to ambient PM characteristics. The method, unlike traditional high temperature measurement methods, applies initial cooling of the flue gas by diluting with clean air inside an inert tunnel to mimic plume conditions. The source dilution approach allows for atmospheric transformation processes for the PM and thus provides ambient-comparable source signature profiles for source apportionment modeling. At present, fine PM data from industrial sources are limited and often not representative of reality, being derived from high temperature source measurement techniques.

Research is being co-sponsored by two Canadian utilities, Environment Canada with the objective of examining source PM characteristics from the electric power generation sector. Two prototype samplers have been developed for the combustion units having low stack velocities (<5 m/s) and medium velocities (<10 m/s). The larger sampler is being retrofitted for field measurement on utility-scale boilers. The basic sampling protocol involves dilution of flue gas with purified air by 20 to 40 times inside a dilution chamber maintained at a 40% relative humidity (RH) to allow for cooling and simulation of atmospheric transformation processes. Portions of the diluted gas are withdrawn, while maintaining isokinetic sampling, through selected cyclone and impactor inlets and filter packs to collect the PM fractions. The method provides mass concentrations of $PM_{2.5}$, PM_{10} and total PM and their size and chemical composition information. To date, fine PM emissions from the combustion of No. 2 and No. 4 heating fuels and pulverized coal have been determined and characterized using the two samplers. The paper summarizes the preliminary size and chemical characteristic data from the combustion of three experimental fuels.

Experimental

Fuels and Combustion Systems. A commercial No. 2 type, petroleum distillate oil was fired in a residential scale, 30 kW hot water boiler, Utica boiler Model Starfire 3. The ultimate analysis of the heating fuel showed 86.7% carbon, 13.5% hydrogen, 0.2% sulphur and 0.07% nitrogen, by mass. A larger oil-fired unit, 130 kW input capacity Weil-McLain Model 478, was used for burning the No. 4 type residual fuel oil. The fuel has 86.5% carbon, 12% hydrogen, 0.7% sulphur and 0.02% nitrogen. A western Canadian sub-bituminous coal blend was supplied by a utility for the combustion experiments on a 0.7 MW_{th} pilot-scale research boiler. This boiler, a smaller model of a full-scale boiler, with its unique burner configurations can provide time-temperature profiles and typical ash behaviour of full-scale units. The coal blend has 9.6% moisture, 11.3% ash, 32.2% volatile matter and 56.5 fixed carbon. The ultimate analysis showed, 69% carbon, 4% hydrogen, 0.9% nitrogen and 0.2% sulphur. These combustion systems are fully equipped with fuel conditioning systems, continuous emission analyzers, temperature and pressure measurement devices and computer controlled data monitoring systems.

Combustion and Emission Measurement Procedures. The preparation of test facilities and experimental procedures for the combustion units have been reported elsewhere[3-5]. Normally the protocols require initial pre-warming of the units and calibration of the analyzers, followed by continuous monitoring of gaseous concentrations O_2, CO_2, CO, NO_x and SO_2 in the flue gas. The fine PM measurement was performed using the source dilution samplers when the experimental conditions were stabilized. An outline sketch of the source dilution sampler is shown in **Figure 1**. The sampling procedures for the units have been optimized and reported in previous publications [4-6].

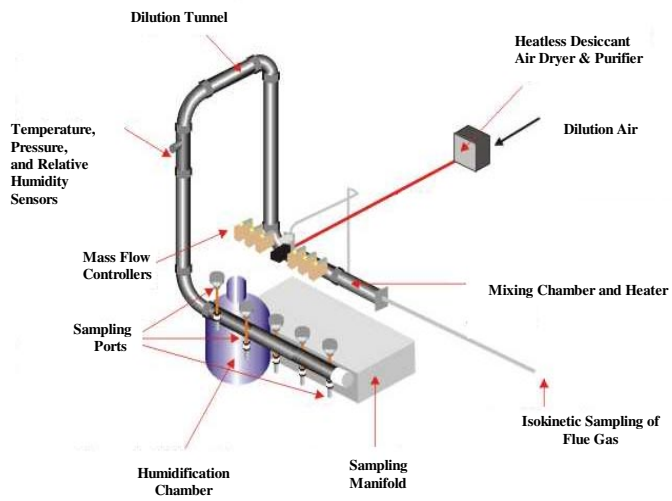

Figure 1. Source dilution fine PM measurement system.

PM Characterization Methods. The characterization protocol for the PM fractions has been published elsewhere [6]. Attention was given to ensure that the analytical techniques applied are comparable to those used in the analyses of ambient PM samples. The CCSEM (computer controlled scanning electron microscopy) was replaced with TEM (transmission electron microscopy) for examining size characteristics of the PM from No. 2 fuel combustion due to their extremely small size.

Results and Discussion

Size Distribution and Morphology. Typical CCSEM particle size analysis provides PM distribution expressed in terms of volume, corrected aerodynamic mass and number. A sample illustration for the No. 4 fuel is shown in **Figure 2**. Results from the multiple runs using five No.4 fuel blends, although not reported here, showed that this residual type fuel emits particles mostly made up of PM_{10} , about 85-90%. These particles are mainly carbon rich with sulphur being the second most abundant element detected. Coal fly ash samples showed

over 90% of PM_{10}, while the particles are Al and Si rich. In both types the presence of other trace elements such as V, Ni, Fe, Ca, Na and Ni are found although coal ash contains significantly higher mineral contents than the oil PM. However, the PM from the combustion of No. 2 fuel is predominantly in the 0.05µm range, thus requiring TEM analysis. The particles are mostly carbon and exist in the form of branched chain agglomerates and clusters. No measurable amounts of mineral matter are detected.

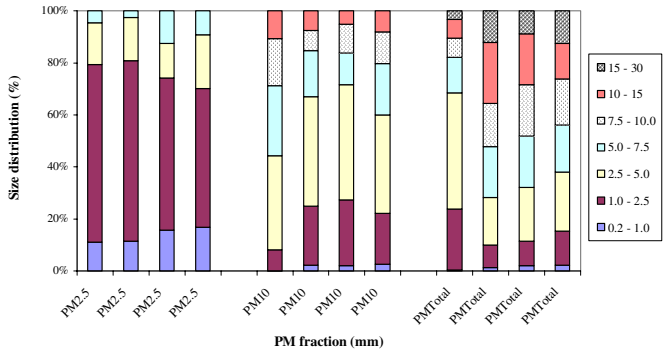

Figure 2. PM Size distribution from No. 4 fuel oil combustion. 0.7% sulphur, 40% RH, 26x dilution

PM Mass Concentrations. Filterable PM mass data is determined by gravimetric analysis using Teflon filters that are pre-conditioned in a control chamber maintained at 40% RH. Results are expressed in terms of particle mass in milligram per cubic metre of dry flue gas at standard temperature and pressure. As expected, the total PM fraction shows the highest mass, followed by PM_{10} and $PM_{2.5}$ in descending order for the test fuels, with the exception of No. 2 fuel. The mass data for No. 4 fuel revealed that the particles contain about 75-90% PM_{10} and 50-70% $PM_{2.5}$. Preliminary research data for the sub-bituminous coal showed that fly ash samples at the ESP exit, contain about 80-85% PM_{10} and 30-50% $PM_{2.5}$. However, the No. 2 fuel PM mass concentrations are similar for all size fractions, suggesting that they are all the in the $PM_{2.5}$ range. The reproducibility of results for No. 4 fuel combustion is very good, with relative standard deviation of less than 5%. Emission sampling for pulverized coal and No. 2 fuel are inherently more difficult due to the sticky nature of fly ash and the very low concentrations from clean-burning distillate fuels. The reproducibility for these results is about 5-15%.

Chemical Species and Simple PM Mass balance. The PM from stationary combustion sources generally contains carbonaceous species, mineral matter and condensed acidic compounds such as sulphates and nitrates. Replicate samples of filterable PM fractions are analysed for trace elements, organic carbons, elemental carbons and sulphates using the established analytical scheme [6]. The results showed up to 86% of mineral matter in the fly ash with about 5% carbons and 3% soluble sulphates. Trace elements are preferentially enriched in the $PM_{2.5}$ fraction. Trace elements, carbons and soluble sulphates exist in the order of 10-12%, 50-90% and 20-40% respectively for the No. 4 fuel. The No. 2 fuel generated PM contains about 20-30% carbons, 40-50% sulphates and 20-30% water that exists as water of hydration associated with sulphate. It should be noted that these percentages would change when fuel sulphur content is varied. The PM speciated mass data for each fuel was reconstructed following simple assumptions used in ambient PM monitoring. The data in Table 1 indicates comparable mass concentrations between gravimetric analysis and the composite data. This information is necessary in developing PM source characteristic profiles for mathematical source apportionment modelling.

Table 1. PM mass balance of experimental fuels (mg/m^3) 40x dilution, 40% R.H.

Fuel		$PM_{2.5}$	PM_{10}	PM_{Total}
0.05%S Diesel 30 kW Boiler	Metal as oxides	0.03	0.02	0.02
	Organic carbon	0.71	0.71	0.68
	Elemental carbon	1.00	1.03	1.03
	Sulphate & Hydration	0.57	0.51	0.51
	By composition analysis	**2.31**	**2.27**	**2.24**
	By gravimetry	**1.93**	**2.09**	**2.09**
0.2%S #2 Fuel 30 kW Boiler	Metal as oxides	0.10	0.09	0.09
	Organic carbon	1.24	1.27	1.12
	Elemental carbon	0.69	0.73	0.76
	Sulphate & Hydration	4.69	4.90	5.76
	By composition analysis	**6.72**	**6.99**	**8.06**
	By gravimetry	**9.76**	**9.86**	**9.80**
0.7%S #4 Fuel 130 kW Boiler	Metal as oxides	2.77	4.89	5.50
	Organic carbon	13.10	14.81	12.44
	Elemental carbon	4.22	11.65	14.27
	Sulphate & Hydration	10.10	10.73	12.73
	By composition analysis	**30.19**	**42.08**	**44.94**
	By gravimetry	**34.23**	**43.54**	**50.33**
0.23%S Bituminous C Coal 0.7 MW Boiler	Metal as oxides	31.00	86.00	99.00
	Organic carbon	3.00	4.00	4.00
	Elemental carbon	0.00	0.00	0.00
	Sulphate & Hydration	2.00	2.00	2.00
	By composition analysis	**36.00**	**92.00**	**106.00**
	By gravimetry	**38.00**	**77.00**	**91.00**

References

(1) Canada Wide Standards. For PM and Ozone; *Canada Gazette*, Part I, Vol 134, No. 22, May 27, 2000, pp 1343-1645.

(2) *Fed. Regist*. 62 FR38652, July 1997.

(3) Lee, S. Win; Whaley, H.; Pomalis, R.; Wong, J.K.L. *ASME, EC*-Vol. 5. **1997**, 97-105.

(4) Lee, S. Win; Kan, B.; Pomalis, R. In: *Proceedings of 5th International Conference on Clean Air and Combustion Technology,* Lisbon, Portugal, July 12-15, 1999.

(5) Lee, S. Win; Pomalis, R.; Kan, Betty. *Fuel Process. Technol*. **2000**, *65-66*, 189-202.

(6) Lee, S. Win. J.Air & Waste Manage. Assoc. **2001**, *51*, 1568-1578.