SME Annual Meeting
Feb. 27 - Mar. 02, 2022, Salt Lake City, UT

Preprint 22-080

DETECTION AND CHARACTERIZATION OF NANOPARTICLES IN RESPIRABLE COAL MINE DUST

S. Assemi, Univ. of Utah, Salt Lake City, UT
T. Akinseye, Michigan Tech. Univ., Houghton, MI
F. Sime, Univ. of Utah, Salt Lake City, UT
X. Wang, Univ. of Utah, Salt Lake City, UT
L. Pan, Michigan Tech. Univ., Houghton, MI
J. D. Miller, Univ. of Utah, Salt Lake City, UT

INTRODUCTION

Respirable coal mine dust (RCMD) is a complex mixture of carbonaceous and mineral particles with a variation in size and shape. Accumulation of RCMD in the lungs of underground coal miners results in severe respiratory damage and ultimately progressive pneumoconiosis known as the black lung disease. The occurrence of the black lung disease dropped to a low of 2.1% in 1990s but has increased to 3.1% in 2000s [1], prompting more research on coal mine dust mitigation.

In addition to surveying the impact of new mining technologies on the size of generated dust and exposure measurement, a comprehensive characterization of physico-chemical properties of RCMD particles are essential for a better understanding of the adverse health effects of coal mine dust. Such vital factors include particle size, surface charge, morphology, composition, and agglomeration state. The respirable fraction of RCMD, has been designated as particles < 10 µm in diameter, and almost all studies on the RCMD toxicity have focused on micron-sized particles. However, recent toxicological studies have shown that nanoparticles (particles with one dimension less than 100 nm) can have a magnified toxicity compared to the larger particles with the same chemistry [2]. Nanoparticles have a much higher specific surface area compared to the same mass of larger particles and are thus more reactive. Most micron-size particles can be cleared by the body's defense mechanism. However, inhaled nanoparticles can easily deposit in all regions of the respiratory tract and can translocate to vital organs. [2].

Valuable information on size and elemental composition of micron sized RCMD particles has been obtained using electron microscopy, and Energy Dispersive X-ray Spectroscopy (EDX) of individually analyzed particles [3,4]. The method requires that individual particles be counted and measured separately. In addition, often times the smaller particles are adsorbed on the larger particles and are hard to measure or distinguish. Field-flow fractionation is a family of elution and separation techniques [5], where the particles can be separated and analyzed in narrow fractions, and can facilitate the characterization of nanoparticles in RCMD. In this study, Asymmetrical Field -flow Fractionation (AsFlFFF) was used to separate and obtain the size distribution of nano-sized RMCD samples. RCMD samples were collected at different coal mines on polycarbonate (PC) filter papers. The collected samples were initially characterized for size and composition using Scanning electron microscopy (SEM) and Dynamic Light Scattering (DLS). In addition a methodology was developed to analyze the nanoparticles in RCMD using the AsFlFFF. Results obtained from the three techniques clearly demonstrated the presence of nanoparticles in RCMD samples. Nanoparticles with diameter below 100 nm were only detected by AsFlFFF. Data on the size distribution, morphology and elemental composition of nanoparticles in RCMD are presented. The challenges, potential, and limitations of AsFlFFF for RCMD analysis are discussed.

MATERIALS AND METHODS

Samples

RCMD samples were collected from different locations at two underground coal mines using gravimetric dust samplers. The dust sampler used a 10 mm Dorr-Oliver cyclone with an air flow rate of 2 L/min, to separate the respirable fraction (<10 µm) from the coarse fraction (>10 µm). The <10 µm fraction was deposited on a 0.8 mm PC filter.

Scanning Electron Microscopy (SEM)

Sections were cut from the PC filter containing the RCMD sample, and were coated with platinum. SEM images were obtained using a Philips XL40 Environmental Scanning Electron Microscope (ESEM) (Amsterdam, The Netherlands) in the back scattered electron (BSE) mode at a 15–17 kV accelerating voltage. Images were analyzed using the NIH Fiji software.

Dynamic Light Scattering (DLS)

Particles on PC filters were first dispersed in an aqueous surfactant solution. 1 mL of the dispersion was transferred to a cuvette for DLS analysis. A Zetasizer Nano instrument (Malvern, PA, USA) was used for the DLS measurements.

Asymmetrical flow field-flow fractionation (AsFlFFF)

AsFlFFF is a powerful particle separation and elution technique, that belongs to the Field-Flow Fractionation (FFF) family of separation techniques [5]. FFF techniques have been vastly used for the separation and characterization of nanoparticles in environmental and biological samples [6].

In AsFlFFF, the separation takes place in a thin, flat, open channel that is filled only with the carrier liquid. A fluid flow is applied as an external force (field) and perpendicular to the direction of the carrier flow, to push the sample particles towards the lower wall of the channel (accumulation wall). A certain time under the applied field (the relaxation time) allows the sample species to separate according to their diffusion coefficients. The smaller particles will form a cloud closer to the middle of the channel and the larger particles will form a cloud closer to the accumulation wall (Figure 1). After the relaxation period, the laminar flow of the carrier fluid will elute sample particles. The smaller particles will elute first with the faster streams of the laminar flow, and the larger particles will elute later. The result is an elution profile (fractogram) that shows the detector signal versus elution time. The elution profile can then be converted to a size distribution.

AsFlFFF analyses were performed using a Postnova AF2000 system (Landsberg, Germany) with UV detection at 254 nm. PC filter samples containing the RCMD particles were suspended in 2 mL of a surfactant solution, and 100 µL samples were injected into the channel. The sample contained larger particles that were settled and excluded from the AsFlFFF analysis prior to the injection step.

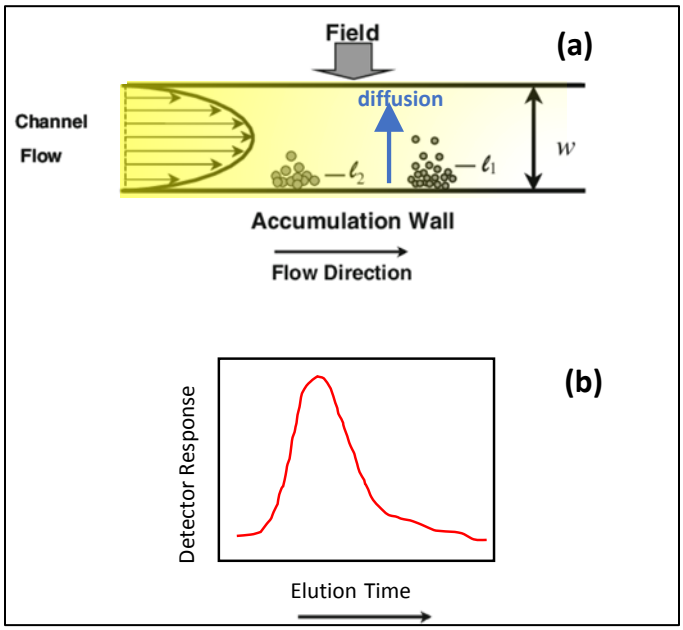

Figure 1. (a) separation in a FFF channel. l_1 and l_2 indicate the sample clouds for larger and smaller sample species. **w** is the channel thickness which is typically 100-350 mm.

RESULTS AND DISCUSSION

A typical SEM image (1000X magnification) of a piece of a polycarbonate filter covered with RCMD is shown in Figure 2a [4]. To obtain the size distribution, each image was processed separately and the particles were counted. The smallest detected particle had an equivalent disc diameter of about 100 nm. Particle size distributions obtained from 30 images (~2000 particles) showed a mode of 230 nm (Figure 2b). A magnification of 50,000 is needed for SEM to acquire images of nanoparticles.

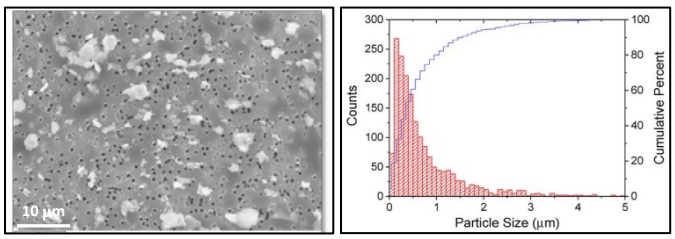

Figure 2. (a) a typical SEM image of a RCMD sample on polycarbonate filter. (b) SEM-based size distribution of RCMD dust samples from a mine (bolter site), showing a mode of 230 nm. Particles under 100 nm were not detected. (Data taken from Ref. 4).

The above process shows that image acquisition and processing can be even more tedious for nanoparticles considering the fact that each particle needs to be analyzed separately for size and composition, and a considerable number of particles need to be analyzed for meaningful and representative data.

Size distributions of the nanoparticles in samples from three locations (Bolter, Miner, Feeder), were obtained by DLS (Figure 3). The results indicate the presence of particles smaller than 1mm. However, DLS is a batch method that is most suitable for the analysis of mono-dispersed, dilute particles. The light scattering signal of particles increases as the 10^6 power of the size. Therefore, signals from the larger particles will mask the signal from the smaller particles.

The elution profile (fractogram) and size distribution of four RCMD sample from a mine in the Eastern United States, obtained by AsFlFFF, showed a size range of 20-300 nm for samples taken from the bolter and miner sites and 40-500 nm for the sample taken from the feeder site. Data for the miner site (sample 2) is shown in Figure 4.

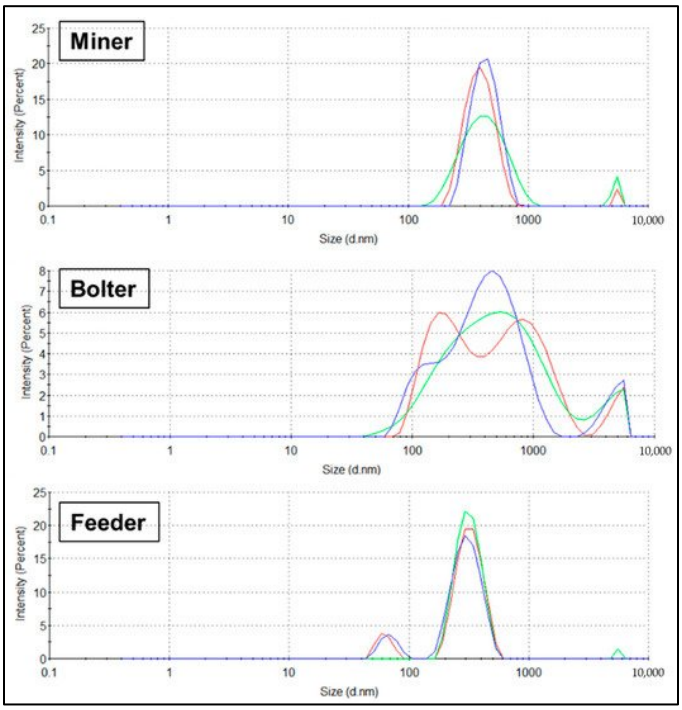

Figure 3. Size distributions of RCMD collected at the miner, bolter, and feeder locations, as determined by Dynamic Light Scattering (DLS) (Data from Ref 4).

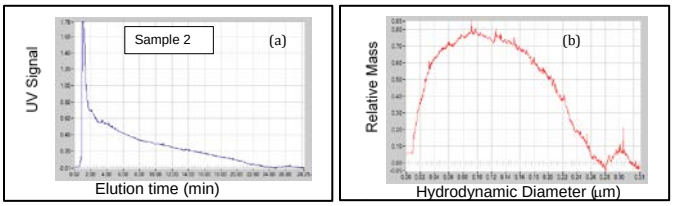

Figure 4. (a) elution profile (fractogram) of sample 2, taken from the miner site of a mine in the Eastern US. (b) Size distribution of the same sample.

It is possible to obtain very narrow-sized fractions (~30 nm) during the elution step of AsFlFFF, for further analyses. Fractions were taken from two locations on the fractogram in Figure 4a and were analyzed by TEM. Size of the nanoparticles in the images corroborated the size obtained by AsFlFFF.

RCMD Samples from a mine in the Western United States were also analyzed by this method. The separation was verified using TEM imaging. For one of the samples, fractions were taken along the size distribution and were analyzed by inductively-coupled Mass Spectrometry (ICP-MS) for major elements (Si, Al, Ca, Mg, Fe) and several trace elements (As, Y, P, Cs, Ce, La, Pb, Se, Hg, U). All major elements showed a higher concentration at the size range below 30 nm. These results indicate a higher positive surface charge and possible higher reactivity for this size range. Concentrations of Se, Hg, Y and As were close to or below the detection limit of the instrument for all fractions. However, U, Cs, La and Ce were detected in the parts per trillion (ppt)range.

CONCLUSIONS

The utility of a AsFlFFF for the separation and analysis of RCMD nanoparticles was investigated. Nanoparticles as small as 10 nm were separated and analyzed using this technique. In addition, fractions were obtained along the size distribution and were analyzed by TEM and ICP-MS. Preliminary analysis of coal samples from two mines (one from the eastern and one from the western US) showed an abundance of nanoparticles in the samples. TEM images (not shown) confirmed the size obtained by AsFlFFF. Analyses of the fractions by

ICP-MS showed the change in the concentration of major and trace elements with size. Preliminary results suggest that particles below 30 nm in diameter can be highly charged and thus more reactive, due to the higher concentration of major cations. The developed methodology still needs to be perfected. However, within limitations, FFF can be helpful in facilitating separation and characterization of nanoparticles (size below 100 nm) in RCMD. A task that is not possible using the present traditional analytical techniques.

FUNDING ACKNOWLEDGEMENT

The authors would like to acknowledge the financial support from the National Institute for Occupational Safety and Health (NIOSH), grant number 75D30119C05527.

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