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Project Report

A Standard Characterization Methodology for Respirable Coal Mine Dust Using SEM-EDX

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Abstract: A key consideration for responsible development of mineral and energy resources is the well-being of workers. Respirable dust in mining environments represents a serious concern for occupational health. In particular, coal miners can be exposed to a variety of dust characteristics depending on their work activities, and some exposures may pose risk for lung diseases like CWP and silicosis. As underscored by common regulatory frameworks, respirable dust exposures are generally characterized on the basis of total mass concentration, and also the silica mass fraction. However, relatively little emphasis has been placed on other dust characteristics that may be important in terms of identifying health risks. Comprehensive particle-level analysis to estimate chemistry, size, and shape distributions of particles is possible. This paper describes a standard methodology for characterization of respirable coal mine dust using scanning electron microscopy (SEM) with energy dispersive X-ray (EDX). Preliminary verification of the method is shown based several dust samples collected from an underground mine in Central Appalachia.

Keywords: Mining; Coal Dust; Respirable; Occupational Health; Particulate Composition; Dust Characterization; SEM-EDX

1. Introduction

A key consideration for responsible development of mineral and energy resources is the well-being of workers. Respirable dust in mining environments represents a serious concern for occupational health. Coal mine dust, in particular, has long been linked to various lung diseases like coal workers pneumoconiosis (CWP) and silicosis [1,2]. Implementation of dust regulations in the US beginning in the late 1960s has significantly decreased overall incidence of such diseases over the past several decades [2–4], but analysis of long-term surveillance data appears to show a recent and unexpected uptick in disease amongst some miners in particular geographic regions like Central Appalachia [3,5–7]. Such trends are alarming considering that most coal mines currently operate below regulatory limits on respirable dust (*i.e.*, particulates with aerodynamic diameter <10 μm), which generally pertain to total mass concentration and crystalline silica content. These trends may suggest that other exposure factors, including specific dust characteristics such as particle composition, size, and shape distributions, may be important in the occupational health context.

While MSHA's new dust rule issued in April 2014 targets further reductions in respirable dust concentrations, it is unclear if or how the lowered limits will affect health outcomes for miners in locations where causal factors for disease are not well understood. The "new dust rule"' was first proposed by the US Mine Safety and Health Administration (MSHA) on 19 October 2010 and was finally issued under the title *Lowering Miners' Exposure to Respirable Coal Mine Dust Including Continuous Personal Dust Monitors* on 23 April 2014 [8]. The rule makes a number of changes to previous regulations on dust limits and sampling in underground coal mines, and specifically will reduce the permissible respirable dust concentration from 2.0 to 1.5 mg/m^3. It will also require use of continuous personal dust monitors (CPDMs) by mine operators, and require that citations be issued in any instances where MSHA-collected samples for single, full shifts exceed the new 1.5 mg/m^3 limit.

Indeed, more comprehensive characterization of coal mine dust is necessary to fully explore these factors. Currently, a standard methodology for comprehensive, particle-level characterization of coal mine dusts does not exist. This paper describes such a methodology, which uses scanning electron microscopy equipped with energy dispersive X-ray (SEM-EDX). Although not commonly applied to respirable mine dust samples, electron microscopy with EDX has proven useful in a variety of environmental and mineral processing/metallurgical applications for fine particulate analysis. It is increasingly being used to specifically understand chemistry and morphology of airborne particulates that represent health hazards—in occupational or ambient environments. For example, methodologies for analysis of nano-sized particulates in around active welding have recently been described [9,10].

A major objective of the method development included optimization of manual analytical efforts—*i.e.*, minimizing the required SEM user time for each sample, while maximizing the range of valuable raw data types to be collected. The developed method includes particle-level analysis of composition, size and shape, from which mass and volume can also be estimated. Construction of automated

spreadsheet program for computational analysis is also described here, as well as preliminary verification of the dust characterization method using three samples collected in the field.

2. Description of Developed Dust Characterization Method

The following sections provide a detailed discussion of the particle characteristics that are included in the developed dust characterization method, as well as a description of procedures used for dust sample collection and preparation, and selection and analysis of specific particles by SEM-EDX. Additionally, computation via an automated analysis program is described for easy analysis of raw data inputs.

2.1. Particle Characteristics of Interest

To fully characterize particles, specific properties are of interest. Particle composition, dimensions, and shape are values which are determined with SEM-EDX, and volume and mass are calculated as a result of the analysis. These particle characteristics provide an abundance of data and information regarding respirable dust samples and aid in the comprehensive analysis of coal mine dust.

2.1.1. Composition

Classification of the dust particles is based on their EDX spectra, which provides a graphical representation of the elements associated with the particle surface. The spectra are generated by detection of X-ray emissions from the particle, caused by interaction of the SEM electron beam with its surface; each element on the particle surface produces a characteristic X-ray when excited by the impinging electrons. Each peak of a spectrum, thus, represents a specific element, and relationships between peak heights can provide some indication of the elemental composition (*i.e.*, minerals can be identified by their atomic stoichiometry). For relatively small particles, such as respirable dust particulates, the electrons may penetrate deep enough into the particle (e.g., to a depth of about 1 μm) to provide relatively good information about its overall composition. However, EDX analysis on small particles is also subject to interference from the sample background (*i.e.*, if electrons penetrate completely through the particle or the electron beam is sufficiently close to the particle edge).

For the developed dust characterization method, considerable effort was aimed at establishing a set of pre-determined compositional categories into which most particles in a coal mine dust sample would be expected to fit. As a preliminary effort, lab-generated dust samples were collected using run-of-mine (ROM) coal, consisting of coal and rock (*i.e.*, primarily shale and sandstone) taken from an underground coal mine in Central Appalachia. The mine is considered "low seam" based on its average coal seam thickness of 24 inches. With an average extraction height of 40 inches, the operation is, thus, cutting about 16 inches of roof and floor rock during coal extraction.

Dust was generated under a fume hood by pulverizing a sample split from the ROM multiple times. For each dust sample collected, a pump was operated at a flow rate of 5 L/min to collect dust onto a 37 mm diameter polycarbonate (PC) filter (0.4 μm pore size), which was positioned near the top of the fume hood, just below the suction fan; this arrangement was deemed appropriate to collect relatively fine dust over short time periods (*i.e.*, 5–10 min) without the use of a cyclone or other size classifier. A cyclone

was not used to collect the laboratory samples, since the primary objectives were simply determination of the ROM mineralogy (*i.e.*, such that appropriate particle composition categories could be identified), and development of standard procedures to be used during the SEM-EDX analysis. For more in-depth investigation of mineralogy, dust samples were also generated by pulverizing approximately pure rock and pure coal sub-samples hand-picked from the ROM.

An FEI Quanta 600 FEG environmental scanning electron microscope (ESEM) (FEI Company: Hillsboro, OR, USA) equipped with a Bruker Quantax 400 EDX spectroscope (Bruker Corporation: Ewing, NJ, USA) was used. In conjunction with the SEM-EDX hardware, the FEI image analysis software and Esprit EDX software provided imaging and graphical spectra results. The ESEM was operated under high vacuum at 15 kV with an ideal resolution and a working distance of approximately 12–13 mm, which was observed to be optimal for this particular scope and application. To prepare collected dust samples for SEM-EDX analysis, filters were removed with clean tweezers, and on a clean, hard surface, a 9 mm diameter trephine (*i.e.*, a cylindrical blade) and a clean razorblade were used to extract the center of the filter. The center sub-section was then attached to an SEM pin-stub mount with double-sided copper tape and sputter coated with gold/palladium (Au/Pd) to generate a thickness of about 10–20 nm (*i.e.*, 60 s sputtering time) and create the conductive surface layer needed for electron microscopy analysis.

Based on detailed analysis of the lab-generated dust samples using a number of EDX parameters, it was determined that twelve elemental peaks should be included in the developed coal mine dust characterization methodology: carbon, oxygen, sodium, magnesium, aluminum, silicon, sulfur, potassium, calcium, titanium, iron, and copper. Further, it was determined that most particles could be classified into six defined categories based on the peak height ratios: "carbonaceous", "mixed carbonaceous", "alumino-silicate", "quartz", "carbonate", and "heavy mineral". Although the ROM dust samples did not contain significant carbonate particles, carbonate particles are expected to be collected in field samples due to "rock dusting" programs in underground coal mines (*i.e.*, applying pulverized inert minerals, such as limestone or dolomite, to coal and rock surfaces underground in order to reduce explosion propagation), For the relatively few particles that could not be classified into one of these six categories, a seventh category "other" was created.

Table 1 provides examples of typical minerals associated with coal mine dust that fall into each of these categories, and defines the rules developed for compositional classification. These rules are fundamentally based on atomic abundance (*i.e.*, atomic percentage equivalencies of primary minerals in each category), which are correlated to the real-time observed peak height ratios (*i.e.*, Cps/eV) on EDX spectra of specific elements for each category. For the purpose of expedient decision making during SEM-EDX use, the observed peak heights are the main parameters used for characterization.

Each of the six defined categories has one or more dominant elements (DEs), which are associated with the mineral(s) represented that category. For a particle to be classified into a given category, the observed DE spectral peak heights must exceed the minimums shown in Table 1. It should be noted that the atomic percentage equivalents shown in Table 1 are operationally defined (*i.e.*, based significant experience of the authors and preliminary analysis of many known particle compositions), and are not representative of stoichiometry expected in the mineral(s) in each category. This is because significant interference from the filter background cannot be avoided for most particles in the respirable size range.

Table 1. Description of dust categories for particle classification by composition.

Dust Category	Example Mineralogy	Parameters for Classification (Atomic % Equivalents)	Real Time Classification (Raw Peak Heights (Cps/eV))
Carbonaceous	Coal	*Carbon* ≥ 70% Oxygen ≤ 30%	*Carbon* ≥ 80 Oxygen ≤ 20
Mixed Carbonaceous	Very thin clay minerals, or clay minerals with some carbon content	4% > *Silicon* ≥ 2% 4% > *Aluminum* ≥ 2% *Carbon* > 70% Oxygen < 20%	20 > *Silicon* ≥ 10 20 > *Aluminum* ≥ 10 *Carbon* ≥ 80 Oxygen ≤ 20
Alumino-silicate	Clay minerals, feldspars	*Silicon* ≥ 4% *Aluminum* ≥ 3% Oxygen > 20%	*Silicon* ≥ 20 *Aluminum* ≥ 20 Oxygen > 20
Quartz	Crystalline silica	*Silicon* ≥ 5% Oxygen > 20%	*Silicon* ≥ 20 Oxygen > 20
Carbonate	Calcite, dolomite	*Calcium/Magnesium* ≥ 5% Oxygen > 20% Carbon < 70%	*Calcium/Magnesium* ≥ 20 Oxygen > 20 Carbon < 80
Heavy Mineral	Pyrite, titanium oxides	*Iron/Titanium/Aluminum ≥ 5%* Oxygen > 20%	*Iron/Titanium/Aluminum ≥ 20* Oxygen > 20
Other	Diesel particulates, *etc.*	Does not fit any of the above	Does not fit any of the above

Note: DE-Dominant element(s) are italicized for each defined category. For particles <1.5 μm in long dimension, DE content can be up to 50% less than the values noted in Table 1 for all defined groups with the exception of "carbonaceous". It was found that the filter media increasingly influences the spectra of smaller particles, with carbon content increasing and DE content decreasing (see below for details).

Indeed, it is well established that particles in this range often produce spectra that are influenced by electron penetration depth and/or electron scattering [11]. Electron penetration depth is generally defined as the depth at which the electron beam can penetrate the sample material. Thus, particles that are very small or thin may produce X-ray spectra that are greatly affected by filter background, and since the developed methodology for dust characterization utilizes PC filters, small particles or those with significant penetration depth are generally observed to exhibit apparently high carbon and oxygen abundances. For example, although crystalline silica particles (SiO_2) should exhibit a silicon and oxygen atomic percentages of roughly 47% to 53% based on stoichiometry, a respirable-sized particle on a PC background may show silicon and oxygen at 10% and 30%—with the balance being attributed carbon. Given the particle sizes in question, it is unlikely that poor liberation between materials (e.g., quartz particles ingrained in carbonaceous dust) is playing a significant role.

To further illustrate, Figure 1 shows the spectrum for a PC filter, which has atomic percentage equivalencies of approximately 85% carbon and 15% oxygen, and Figure 2 shows spectra and actual SEM images of typical "carbonaceous" and "alumino-silicate" particles. The spectra of alumino-silicates should not inherently show high abundances of carbon, but the carbon peak is observed to be very high as an artifact of PC filter interference. The phenomenon of increasing carbon content with decreasing particle size is applicable for all defined dust categories.

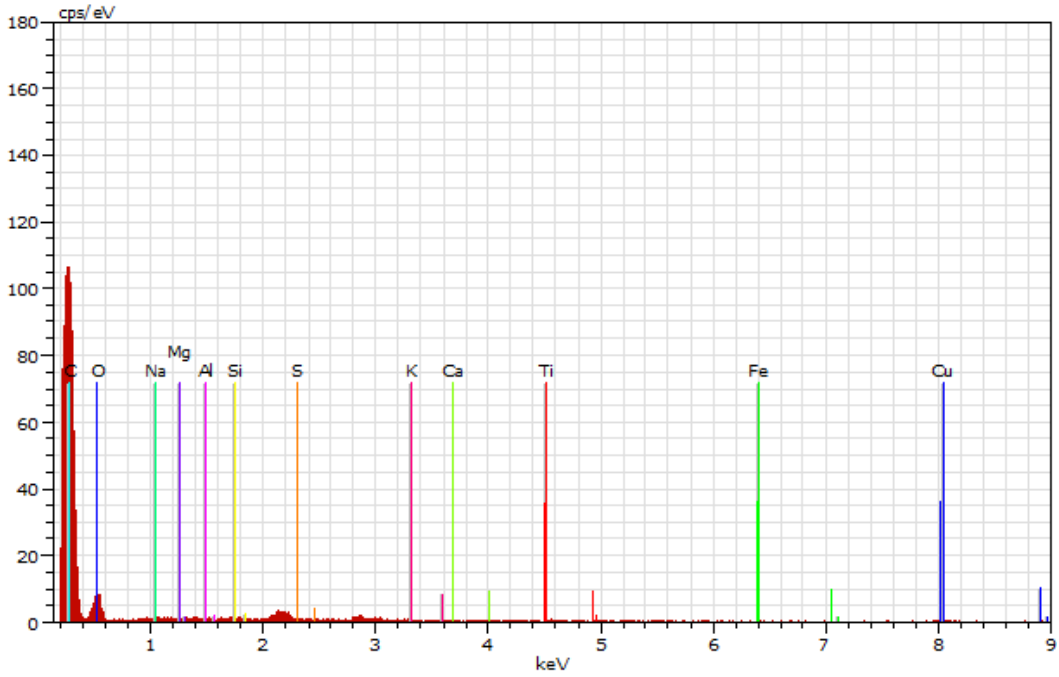
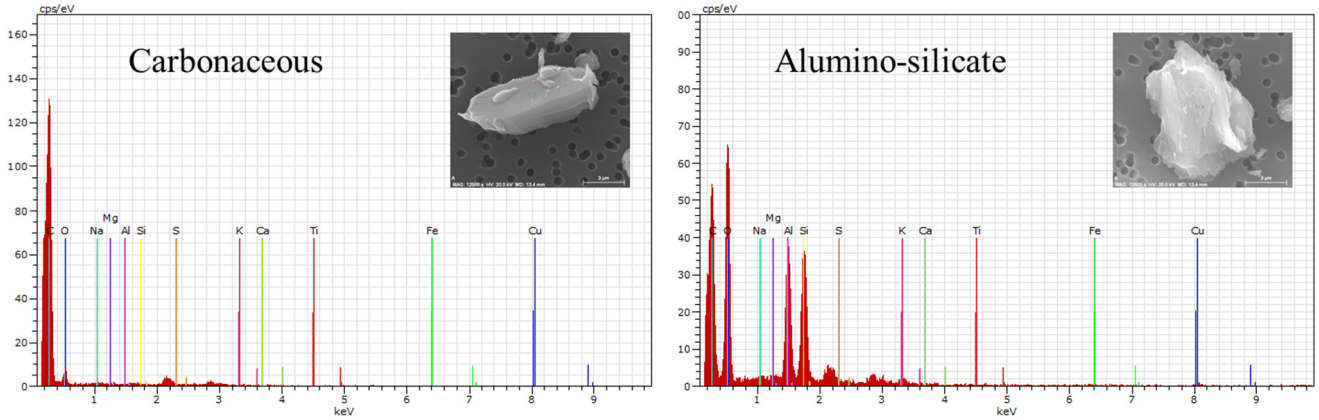


Figure 1. Example spectrum of the PC filter media. The red peak on the left side of the spectrum is the peak associated with carbon, and the peak to the right of carbon is the oxygen peak. The small peaks between 2 and 3 keV are the peaks from the Au/Pd sputter coating, which should be present in all spectra when Au/Pd is used to coat the samples.



(**a**) (**b**)

Figure 2. Comparison of example spectra and images for carbonaceous (**a**) and alumino-silicate (**b**) particles at 12,500× magnification. The spectrum for the carbonaceous particle (L = 9.87 μm) has a relatively large carbon peak and a much smaller oxygen peak, while the spectrum for the alumino-silicate particle (L = 11.24 μm) has relatively large oxygen and carbon peaks, and aluminum and silicon peaks of similar height.

To understand more about the particle size at which electron penetration depth may result in apparently enhanced carbon peaks, an experiment was conducted that examined quartz particles of decreasing size. To investigate, a ROM lab-generated dust sample was collected onto a PC filter. Under the SEM, the filter was scanned for quartz particles of varying sizes. Particles with a long dimension (*L*)

of roughly 0.7 μm, 1 μm, 1.5 μm, 2 μm, 2.5 μm, and 3.5 μm were found, and EDX spectra were observed for each. (*L* is simply the longest dimension visible for the particle, see e.g., [12]). Results showed that carbon peaks were higher for smaller particles; specifically, particles with $L \geq 1.5$ μm had carbon peaks <80 Cps/eV and silicon peaks >50 Cps/eV, while particles with $L < 1.5$ μm had carbon peaks approximately 80 Cps/eV and silicon peaks approximately 20 Cps/eV. Thus, particles with *L* much less than 1.5 μm may have exceedingly small DE peaks; and, the rules for classifying such particles into each compositional category should make allowances for their larger carbon peak due to the probability of electron penetration and/or scatter.

Understanding the carbon content of particles in the "mixed carbonaceous" category is particularly challenging. While their EDX results indicate that these particles have both alumino-silicate and carbonaceous characters, their identity and origin are not definitely known. Several possibilities exist. Most likely, particles classified as "mixed carbonaceous" are actually very thin and platy alumino-silicate particles, which are influenced ever more than other alumino-silicates by electron penetration. This prospect is supported by other recently published work by the authors [13]. Another possibility is that mixed carbonaceous particles may actually be alumino-silicates that are coated with ultrafine coal dust. Finally, it cannot be ruled out that this category could include clay mineral particles with some biogenic component, which seems possible considering the diagenesis of coal and surrounding sedimentary rock formations such as black shales.

To determine the minimum carbon content that permits classification into the mixed carbonaceous category, an experiment was conducted that looked at dust particles on a copper background media; the copper tape ensured that any electron penetration would not result in an enhanced carbon peak, but rather in copper peaks. This experiment was aimed at determining if EDX spectra from "mixed carbonaceous" particles actually exhibited high carbon peaks due to their composition, or if such peaks are simply an artifact of significant electron penetration. An ROM dust sample was collected on a PC filter, and then some of the dust particles were transferred onto copper tape and prepared for SEM analysis by the usual sputter coating routine. Particles with $L > 5$ μm whose EDX spectra exhibited relatively high aluminum and silicon peaks were specifically studied. Upon analysis of 30 such particles, only four spectra were found to have carbon peaks >80 Cps/eV. These results indicate that, in most cases, the high carbon content in "mixed carbonaceous" particles is related to interference from the PC background.

2.1.2. Dimensions

The long (*L*) and intermediate (*I*) dimensions of any particle analyzed can be determined directly from the SEM images using standard "line measurement" tools included in the SEM imaging software. *I* is the longest dimension perpendicular to *L*, which was defined above, in the same plane [12]. Following direct measurement of *L* and *I* (in μm), the short or third-dimension (*S*) can be estimated. Theoretically, *S* is the length dimension of a particle measured at a right angle to the plane in which *L* and *I* have been found; so *S* essentially describes particle thickness. Since different minerals have characteristic shapes, a unique ratio between *S* and *I* can usually be defined for a given mineral type. The unitless *S:I* ratio (*R*) is similar to the aspect ratio generally used in the field of sedimentology (e.g., see [14]). Alumino-silicate particles, for example, tend to be relatively flat with relatively small *R* values, whereas

quartz particles tend to be thicker with higher *R* values. Thus, based on the compositional classification of each dust particle by EDX and its measured *I* value, an *S* value (in μm) can be estimated by Equation (1):

$$S = R \times I \quad (1)$$

For the particle characterization methodology developed here, the *R* values assigned to each of the six defined compositional categories of interest are as follows: 0.6 for carbonaceous, 0.5 for mixed carbonaceous, 0.4 for alumino-silicate, 0.7 for quartz, 0.7 for carbonate, and 0.7 for heavy minerals. These constants are based on those commonly used in the field of sedimentology and extensive experience of the authors in electron microscopy analysis of mineral particulates. The mixed carbonaceous category *R* value is an average of the carbonaceous and alumino-silicate values since the identity of these particles is not definitively known. Dust characterized as "other" cannot be assigned an *R* value.

2.1.3. Shape, Volume, and Mass

A variety of shape factors can also be computed for particles, including a measure of maximum projection sphericity (Ψ_p), and the cross-sectional (d_c) and spherical (d_s) diameters. The Ψ_p value can be determined from the *L*, *I* and *S* dimensions using Equation (2), which was derived by Sneed and Folk (1958). Ψ_p is a dimensionless quantity and values range between 0 and 1; values that approach 1 are associated with particle shapes that are increasingly spherical (*i.e.*, *L*, *I*, and *S* are very similar), whereas values that approach zero are associated with particle shapes that exhibit relatively small *S* dimensions as compared to *L* and *I* [12]. The d_c and d_s values (in μm) can be computed from Equations (3) and (4), respectively. The cross-sectional diameter is the only calculated value based entirely on measured properties of particle size and is only accurate if the particle is a perfect sphere. The spherical diameter is more commonly used and is considered a better approximation of the particle size in aerodynamic applications [15]. Further, the spherical volume (*V*) can also be computed (in μm^3) from Equation (5). By assigning approximate density values (ρ) to each compositional category, the particle masses (*m*) can additionally be estimated (in μg) using Equation (6). Based on average densities for the primary minerals expected in each of the six defined compositional categories (*i.e.*, see [16]), the following ρ values (in g/cm^3) have been assigned: 1.4 for carbonaceous, 2.0 for mixed carbonaceous, 2.5 for alumino-silicate, 2.6 for quartz, 2.7 for carbonate, and 4.0 for heavy minerals. The mixed carbonaceous class density is an average of the carbonaceous and alumino-silicate class densities.

$$\Psi_p = \left(\frac{S^2}{L \times I}\right)^{1/3} \quad (2)$$

$$d_c = \frac{L \times I}{2} \quad (3)$$

$$d_s = \Psi_p \times L \quad (4)$$

$$V = \frac{4}{3} \times \pi \times \left(\frac{d_s}{2}\right)^3 \quad (5)$$

$$m = V \times \rho \times 10^{-6} \quad (6)$$

In addition to the shape factors noted above, particle angularity might also be considered. Angularity is an effective measure of the sharpness of the edges of a particle and, in the context of coal mine dusts,

may be important in controlling interactions between respired particles and lung tissue. Angularity can be rigorously determined by measuring the observed angles of particles on SEM images; however, particularly for small particles (*i.e.*, with $L \leq 5$ μm), such analysis would require significant time. Given that a stated goal of the dust characterization method developed here was to efficiently collect data, it was, therefore, decided that a qualitative evaluation of angularity should be employed; practically, this allows for collection of some potentially valuable information without requiring excessive analytical time. This type of classification of angularity has historically been applied to particles in the micrometer size range [17,18]. To qualitatively describe angularity, particles selected for characterization should be classified as rounded (*r*), transitional (*t*), or angular (*a*) by the SEM user, see Figure 3 [19].

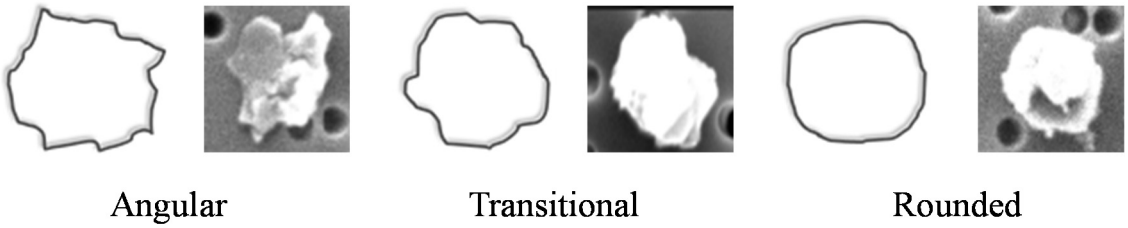


Figure 3. Angularity classification categories based on the qualitative analysis of the sharpness of particle edges.

2.2. General Procedures for Dust Characterization

In order to successfully analyze samples in a methodical manner, the collection, filter preparation, and analytical process should be sound. The following steps are outlined to provide the user with a detailed protocol to efficiently and effectively characterize respirable dust samples.

2.2.1. Sample Collection and Filter Preparation

For collection of respirable dust samples in the field for SEM-EDX analysis, an appropriate pump deemed permissible for use in underground coal mines must be used; at present, the MSA Escort ELF pump is almost exclusively used for such applications because it has the capability to maintain near constant flow rate under a variety of environmental conditions [20]. To ensure collection of only respirable dust particles and, thus, rejection of particles above the respirable range, the pump should be operated with a cyclone at a flow rate between about 1.7–2.2 L/min [21], such that the cyclone median cut point is 4 μm according to the NIOSH 0600 method of sampling [22]. While compliance dust samples used for determining respirable mass concentration are generally collected on pre-weighed PVC filters, samples to be analyzed by SEM-EDX should be collected on PC, because they provide a suitable substrate (*i.e.*, background media) for electron microscopy [11,23,24]. Filter cassettes should be unassembled two or three-piece types, such that the filters can be easily removed from the cassette for analysis.

In preparing the dust samples for SEM-EDX analysis, filter cassettes are carefully unassembled and the filters are removed with clean tweezers. On a clean surface, a 9 mm diameter trephine and a clean razorblade are used to extract the center of the filter. The sub-section removed for analysis represents approximately 6% of the 37 mm filter. It is recognized that particle uniformity as a function of particle size may be variable for these types of filters, which can result in larger particles depositing toward the

center [25]; yet deposition is fairly radially symmetric [26]. Center filter analysis has been shown to provide reasonably precise results for field samples using two or three-piece cassettes [26]. As the main objective here is to provide relative comparisons between center filter sub-sections, some work has been completed to demonstrate that particles >0.5μm are uniformly distributed by number across the sub-section.

This filter sub-section is then attached to an SEM pin-stub mount with double-sided tape (e.g., copper, carbon), and sputter coated with gold/palladium (Au/Pd) to create the conductive surface layer needed for electron microscopy analysis. It should be noted that carbon sputter coating cannot be used since this will interfere with composition analysis by EDX of the dust particles containing carbon, but other sputter coatings (e.g., platinum, Pt) might be considered. During development of the characterization method, it was observed that a coating thickness of about 10–20 nm (*i.e.*, 60 s sputtering time) was optimal for preventing sample charging while allowing sufficient electron interaction with the dust particles to provide high-resolution SEM images and EDX spectra.

2.2.2. Particle Selection and Analysis by SEM-EDX

Following dust sample collection and filter preparation, SEM-EDX is used for particle characterization. Although equivalent equipment could be used, for the method outlined in this paper the same equipment and software, described above, was utilized. The developed method utilizes images obtained from a secondary electron (SE) detector for physical characterization of the dust particles (*i.e.*, to measure dimensions and qualitatively evaluate particle angularity), and EDX spectra for compositional analysis.

In order to select particles for characterization without bias, a rigorous routine was developed to navigate the prepared 9 mm diameter filter sub-sections under the SEM. The routine was developed using an iterative process, whereby over 700 particles in total from the lab-generated dust samples were interrogated for elemental composition, long and intermediate dimensions and estimated shape factors (all described in detail below). With each iteration of analysis, the routine was improved until nearly all particles encountered could be quickly classified into one of the pre-determined compositional categories described above using the EDX spectra, and raw size and shape data could be efficiently gathered for later computational analysis. It is important to note that this routine was developed based on the assumption that somewhere between 50 and 150 particles would be analyzed per dust sample, with fewer particles limiting the statistical power of results and more particles limiting practicality due to time requirements. During preliminary verification of the dust characterization method, a simple evaluation of the effect of number of particles analyzed (*i.e.*, statistical sample size) on resulting compositional distribution was conducted (see below). Ultimately, it was determined that analyzing 100 particles per sample provided enough information about the sample while maintaining reasonable analytical time requirements (*i.e.*, about 75–90 min per sample). A detailed description of the particle selection and analysis routine follows.

First, the SEM should be focused at a magnification of 10,000×, which will allow for analysis of particles within the desired size range (*i.e.*, about 0.5–8 μm); a somewhat higher magnification could be used if the particle size distribution is relatively small (*i.e.*, there are few large particles), but significantly lower magnification will prohibit adequate resolution for analysis of finer particles. With the line measurement tool, two horizontal lines are then drawn 2 μm apart and spanning the entire width of the screen, such that the space between the lines is centered on the screen (Figure 4). The SEM is then

positioned such that the dust characterization will begin in the top left-hand portion of the prepared filter subsection, approximately three screen shifts from its outer edge and approximately 2.25 mm from the top (*i.e.*, one quarter of the diameter) (Figure 5). Three screen shifts from the edge of the filter prevents analysis of any particles disturbed during the filter sub-sectioning process. Additionally, the placement of the SEM stub inside the instrument determines the orientation of the "top" of the stub, based on the upper border of the screen.

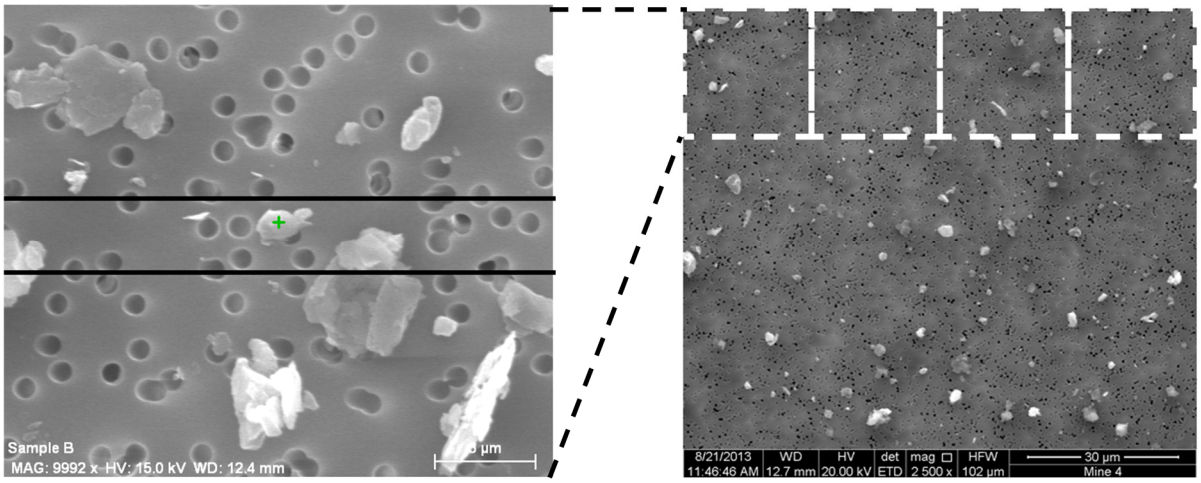


Figure 4. Example of particle selection and screen shifting via the joystick. The image on the left illustrates analysis of particles intersecting between the two lines in the center of the screen at 10,000× magnification. The image on the right, at 2500× magnification, shows four screens, each outlined in a white dotted line, where analysis (at 10,000× magnification) will take place consecutively.

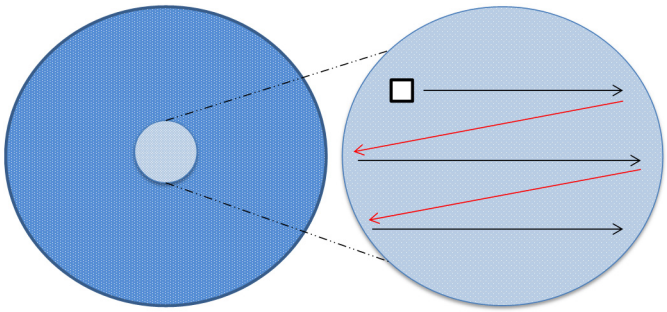


Figure 5. Illustration of 9 mm diameter filter sub-section and navigation routing for SEM-EDX analysis. The image on the left is the whole 37 mm diameter filter and the image on the right depicts the sub-section removed for analysis. The box in the top, left corner of the filter sub-section illustrates the first frame (*i.e.*, field of view) in which particles should be selected for characterization; the black arrows in the filter sub-section define the directions for successive screen shifts between characterization frames. When one horizontal line of analysis is complete (black arrow directions), the red arrows define shifting back to the left side of the filter to continue analysis.

Once the instrument is focused and initially positioned, selection and analysis of dust particles can begin. Moving from left to right on the screen, each particle with $L > 0.5$ µm that intersects the space

between the two horizontal lines and falls completely within the field of view should be selected for analysis; if no particles in the field of view fit these criteria, the next field to the right can be examined, and so on (see below.) Particles with $L < 0.5$ μm are too small to produce quality spectra results—if analysis of smaller particles is critical, transmission electron microscopy (TEM) would be better suited for this application [27]. In an effort to analyze more of the filter area, in regards to high dust density samples, a maximum of 10 particles (*i.e.*, the first 10 that meet the above criteria moving from left to right) per field of view should be analyzed. This would allow a minimum of 10 fields of view in order to characterize 100 particles.

At the approximate center of each particle selected for analysis, the "spot" (or analogous) analysis function on the SEM software can be used with in conjunction with the EDX software to generate elemental spectra. Based on the rules outlined in Table 1, the particle can be classified into one of the seven compositional categories. Additionally, the L and I dimensions of each selected particle should be measured using the built-in line measurement tools in the SEM software. Finally, angularity should qualitatively be classified into one of the three categories described above (Figure 3). After recording raw data (*i.e.*, L, I, angularity, and composition), the user can proceed to the next particle selected for analysis. Once all eligible particles (*i.e.*, based on the criteria above) in the current field of view have been analyzed, the user should proceed to the next field of view (*i.e.*, moving to right per Figures 4 and 5) for selection and analysis of more particles.

The above steps should be followed until analysis reaches the right-hand side of the filter subsection, approximately three screen shifts from its edge, or until 100 particles have been analyzed, whichever comes first. If 100 particles have not yet been analyzed, the user should navigate back to the left side of the filter subsection (see top red arrow in Figure 5), and reposition the sample such that the field of view is approximately three screen shifts from the outer edge of the filter subsection and approximately 4.5 mm from the top (*i.e.*, half of the diameter). From this position, particles should again be selected for analysis by scanning from left to right within the current field of view and adhering to the criteria outlined above; then, analysis should proceed to the next field of view. If the user again reaches the right side of the filter subsection before 100 particles are analyzed, the SEM can be repositioned back to the left—this time approximately three screen shifts from the left edge of the filter subsection and approximately 6.75 mm from the top (*i.e.*, three-fourths of the diameter). Particle selection and analysis should proceed as before.

2.3. Automated Analysis Program

To automate analysis of the raw data collected from SEM images and EDX spectra, a spreadsheet program was also developed using Microsoft Excel 2010 (Microsoft, Redmond, WA, USA). For each dust particle, the user inputs the compositional classification (*i.e.*, per Table 1), measured dimensions (L and I), and qualitative angularity classification (*i.e.*, r, t, or a), and the program then computes the following characteristic quantities based on the assigned R and ρ values for each compositional category and Equations 1-6: short dimension (S), maximum projection sphericity (Ψ_p), cross-sectional diameter (d_c), spherical diameter (d_s), volume (V), and mass (m). Subsequently, distributions of composition, size (*i.e.*, d_s), and angularity (either by particle number or mass) can be automatically generated for each dust sample. While composition and angularity classifications are inherently categorical (*i.e.*, each particle has been

placed into a specific composition or angularity category by the SEM-EDX user), particle size is continuous (*i.e.*, the computed spherical diameter is numeric quantity.) Thus, to generate distributions of quantities based on particle dimensions, a number of size categories (or classes) was defined; for this, a logarithmic base-2 scale was uses, which is a common approach used to classify particles based on work done by Wentworth (1922) [28]. Here, the automated program considers a total of nine size classes from >0.125 μm to >16 μm.

The spreadsheet program additionally includes input cells for general sample information (e.g., sample name or number, description of collection location or conditions, total filter area and filter sub-section area, total number of particles characterized, total linear length of filter analyzed), and provides basic output based on that information (e.g., percent of total filter analyzed, approximated particle density on the sub-section by mass or number). A number of graphical representations of the data results are also generated for each sample.

3. Preliminary Verification of Developed Characterization Method

In order to provide some preliminary verification of the characterization method developed for coal mine dust by SEM-EDX, three field samples were collected and analyzed according to the guidelines outlined above. In particular, the objectives were to: (1) verify that analysis of 50–150 particles per sample is sufficient to describe the compositional, size, and shape distributions on the filter sub-sections; and (2) verify that the six defined compositional categories using the lab-generated dust samples from ROM material, and rules for classification of particles into each category do, indeed, allow characterization of the majority of particles from real field samples (*i.e.*, do most particles fit into one of these categories, or are many particles being classified as "other"?)

It should be noted that the question of particle distribution was briefly addressed in Sellaro and Sarver, 2014. In summary, particle quantification was completed on four different areas (at 2500× magnification) of filter sub-sections from 17 field samples; this involved counting all particles with L dimensions >0.5 μm in each of the four areas, which were each located in a different quadrants of the filter sub-section. Particle counts were determined to be similar (*i.e.*, based on a 95% confidence interval) between each of the four areas for all but two samples. These specific filters had one quantification area with many agglomerated particles, as opposed to few, separate particles, viewed on the other three quantification areas. The agglomeration in these samples is thought to be due to humidity throughout the intake airway of the mine, where both were collected [29].

3.1. Materials

Three dust samples used for method verification were collected from the same underground coal mine where the ROM sample used for method development originated. An Escort ELF pump with a Dorr-Oliver cyclone was used to collect the samples onto 37 mm PC filters, and each sample was collected over a period of about 120 min. The first sample, "Roof Bolter", was collected from a location adjacent to a roof bolting machine, and thus was expected to contain relatively high proportions of alumino-silicate, and possibly quartz particles (*vs.* other compositions), due to the drilling activity of the machine into roof material. The second sample, "Belt Drive", was collected from a location just above a belt drive, where coal and rock were being transported below on a conveyor belt. The "Belt Drive" sample was

anticipated to include greater proportions of carbonaceous particles, and some carbonate particles were also expected due to heavy rock dusting in the belt entries. (Rock dusting is a practice used to limit propagation of coal dust explosions, and requires walls and floors to be covered with fine inert material such as $CaCO_3$). The third sample, "Intake", was collected from a location near the working section of the mine in intake air (*i.e.*, fresh air being delivered to the mine by its ventilation system). The "Intake" sample was expected to have relatively similar proportions of carbonaceous and alumino-silicate particles, with some carbonate due to rock dusting in the area.

Estimated particle densities on the Roof Bolter, Belt Drive, and Intake filter sub-sections were 16,292 particles/mm^2, 12,639 particles/mm^2, and 1850 particles/mm^2, respectively. These densities were extrapolated from the average number of particles counted in four different areas on each sub-section; each area was 10,404 μm^2 and located in a different quadrant of the sub-section areas. Figure 6 displays SEM images for each sample.

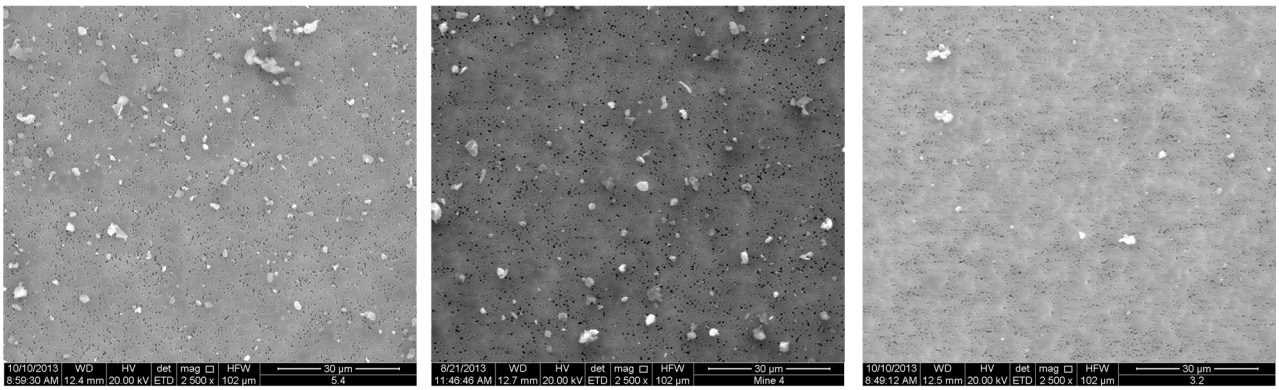


Figure 6. SEM images at 2500× magnification for the filter sub-sections from each verification sample showing relative particle densities. The far left image represents the "Roof Bolter", followed by the "Belt Drive" image, and finally the "Intake" image on the right.

3.2. Results and Discussion

To evaluate the effects of number of particles analyzed (*n*) on dust sample characterization results, compositional distributions by particle number and mass were compared for a range of *n* values (Table 2). For the Roof Bolter and Belt Drive samples, 200 particles in total were analyzed, and the resultant compositional distributions were compared for the first 25, 50, 100, 150, and 200 particles (*i.e.*, *n* = 25, 50, 100, 150 or 200); for the Intake sample, only 100 particles were analyzed in total, so *n* values of 25, 50, and 100 were compared. Somewhat surprisingly, when comparing compositional distribution of particles by number, all samples showed relatively similar results across all *n* values—meaning that even when *n* was increased 4- or 8-fold, little change was observed in the relative number of particles being classified into each compositional category.

When comparing compositional distribution by mass, however, only the Belt Drive sample produced similar results across all *n* values. For the other two samples, as *n* increased, the distributions changed significantly. For example, in the Roof Bolter sample, the first 100 particles analyzed showed very little carbonaceous material on a mass basis, but first 150 particles analyzed showed that over a quarter of the mass was due to carbonaceous particles. This particular discrepancy was traced to a single very large

coal particle (d_s > 5 μm) that was selected for analysis based on the developed dust characterization method, and it underscores a key challenge that aerosol scientists and industrial hygienists often face when studying or reporting on particulates. Indeed, due to limitations in analytical equipment and the efficiency of bulk analyses, environmental monitoring and regulation of airborne particulates is often based on mass rather than number concentrations. This analysis also suggests that in order to obtain accurate estimated mass calculations, a larger number of particles should be counted. The addition of existing automated image and X-ray analysis software could provide this capability.

Table 2. Distribution of particle composition by number (and mass) for the method verification samples. All values are rounded to the nearest whole number, which may result in totals being slightly different than 100%.

Roof Bolter	**25 Particles**	**50 Particles**	**100 Particles**	**150 Particles**	**200 Particles**
Carbonaceous	12% (1%)	12% (2%)	11% (3%)	11% (27%)	12% (21%)
Mixed Carbonaceous	36% (31%)	28% (25%)	32% (19%)	33% (26%)	35% (23%)
Alumino-Silicate	48% (68%)	50% (64%)	49% (67%)	47% (39%)	45% (41%)
Quartz	4% (0%)	8% (7%)	6% (10%)	6% (6%)	7% (8%)
Carbonate	0% (0%)	0% (0%)	0% (0%)	0% (0%)	0% (0%)
Heavy Mineral	0% (0%)	2% (2%)	2% (1%)	3% (2%)	3% (7%)
Other	0% (0%)	0% (0%)	0% (0%)	0% (0%)	0% (0%)
Belt Drive	**25 Particles**	**50 Particles**	**100 Particles**	**150 Particles**	**200 Particles**
Carbonaceous	20% (27%)	24% (40%)	29% (37%)	26% (36%)	24% (27%)
Mixed Carbonaceous	20% (3%)	24% (7%)	21% (5%)	21% (5%)	25% (5%)
Alumino-Silicate	32% (62%)	30% (40%)	30% (46%)	33% (48%)	30% (47%)
Quartz	4% (0%)	2% (0%)	4% (1%)	3% (1%)	5% (2%)
Carbonate	8% (1%)	12% (9%)	12% (10%)	12% (9%)	14% (18%)
Heavy Mineral	16% (7%)	8% (4%)	4% (1%)	5% (1%)	4% (1%)
Other	0% (0%)	0% (0%)	0% (0%)	0% (0%)	0% (0%)
Intake	**25 Particles**	**50 Particles**	**75 Particles**	**100 Particles**	
Carbonaceous	32% (56%)	40% (50%)	44% (44%)	45% (48%)	
Mixed Carbonaceous	20% (2%)	16% (4%)	17% (33%)	16% (30%)	
Alumino-Silicate	40% (22%)	36% (25%)	31% (12%)	32% (14%)	
Quartz	4% (1%)	2% (1%)	1% (0%)	2% (0%)	
Carbonate	4% (19%)	2% (16%)	1% (7%)	1% (6%)	
Heavy Mineral	0% (0%)	4% (4%)	5% (3%)	4% (3%)	
Other	0% (0%)	0% (0%)	0% (0%)	0% (0%)	

In consideration of the results presented in Table 2, and the typical times required for SEM-EDX analysis for different *n* values, it was determined that analysis of 100 total particles per sample should be both sufficient (at least for describing sample distributions by particle numbers) and practical for the developed dust characterization method. Further work may be needed, however, to determine if or how few, relatively large particles in a sample are contributing to its characteristics on a mass basis. If required, simple additional steps could be incorporated into the developed characterization method to quickly gather more data in this regard (e.g., visually scanning the filter sub-section at a relatively lower

magnification to assess density of large particles, or elemental mapping at a relatively lower magnification to assess compositional differences in larger particles).

Additionally, from Table 2, it appears that the six pre-determined compositional categories, and rules outlined in Table 1 for particle classification, can account for most respirable particles in expected in dust samples from underground coal mines. Indeed, of the 500 total particles analyzed across all three samples, none required classification into the "other" category. It should of course be noted that dust composition could vary with varying coal and rock geologies, and mining and operational practices—and, thus, between mines. So, further verification of the developed method for dust characterization should certainly be conducted using samples collected from multiple mines/regions of interest.

To demonstrate the robustness of the developed dust characterization method, size, and compositional distributions (again by particle number and mass) for the three verification samples were generated by the automated spreadsheet program. Figure 7 shows the results for the sample collected adjacent to a roof bolter. With respect to composition, the sample largely consists of alumino-silicates, with significant coal and mixed carbonaceous particles too. These results are consistent with expectations based on the sampling location (*i.e.*, the bolter was drilling into the roof, but the air being moved through the mine also contains coal particles). These results additionally underscore the influence that large particles can have on mass-based data. Figure 7 indicates that 1% of the particles in this sample, which all happened to be carbonaceous, fell into the 4–8 μm size class—but these make up 19% of the total mass. Figure 8 shows the relative angularity of particles in the "Intake" sample. This data indicates that alumino-silicates and mixed carbonaceous particles tend to be primarily angular, while carbonaceous particles can be more rounded.

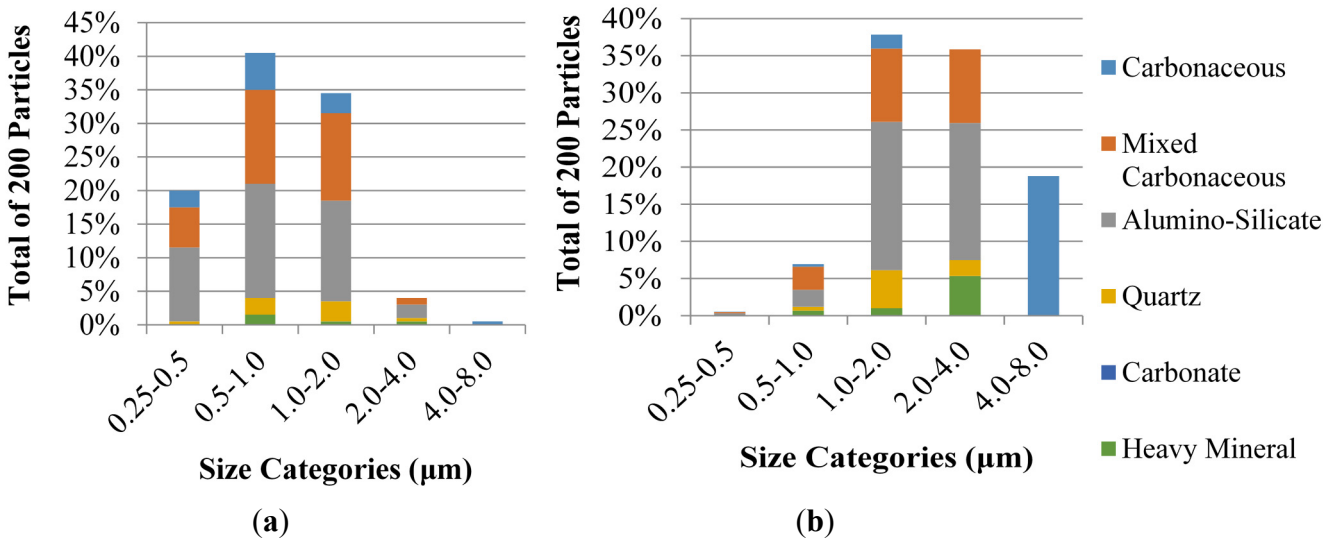


Figure 7. Particle size distribution by number (**a**) and by mass (**b**) for the Roof Bolter sample; the relative number of particles in each compositional category is shown within each bar.

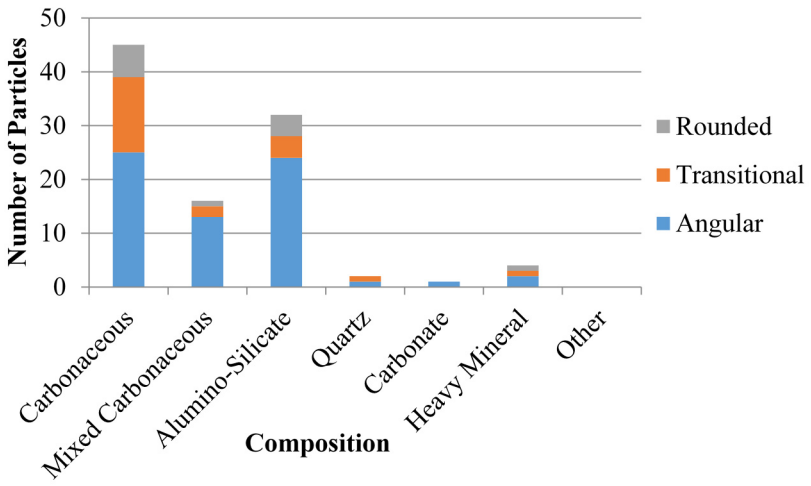


Figure 8. Particle compositional distribution by number for the Intake sample; the relative number of particles classified as having angular, transitional, or rounded shapes is shown within each bar.

4. Conclusions

SEM-EDX is a powerful tool, which can be used for particle-level analysis of dust samples. This paper describes a standard methodology developed for the purpose of achieving more comprehensive characterization of respirable dusts in underground coal mines. Due to the large amounts of data that can be generated by this method, a relatively simple spreadsheet program is recommended for automating computational analyses to compare particles within and between dust samples. The recent availability of automated particle analysis instrumentation to existing scanning electron microscopes could also provide an even more robust analysis capability by increase the number of particles analyzed by at least five to ten fold.

Future work should be geared toward further understanding particle uniformity, by both number and size of particles, across the entire filter area and uniformity by particle size across the filter sub-section. In cases of non-uniformity, such as agglomerated dust, characterization of >100 particles may be necessary. The method is also user specific, and the steps outlined above are at the interpretation of the user, such as in cases of exceptionally high dust density samples and increased numbers of large dust particles. Although the method outlined in this paper was shown to classify particles properly from one specific mine, to accommodate a mine of different mineralogy, the particle dust categories should be altered prior to particle classification. The time required for this type of comprehensive analysis can be a major drawback; however, the use of a standard methodology may increase analytical efficiency, as well as consistency.

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Author Contributions

Rachel Sellaro and Emily Sarver conceived the experiment and methodology. Rachel Sellaro preformed the experiment, and led the data collection, analysis and writing. Emily Sarver provided funding, guidance, and editing to the paper. Dan Baxter provided expertise, insights, and advice regarding particle analysis using SEM-EDX.

Conflicts of Interest

The authors declare no conflict of interest.

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