DEVELOPMENT AND IMPLEMENTATION OF A STANDARD METHODOLOGY FOR RESPIRABLE COAL MINE DUST CHARACTERIZATION WITH THERMOGRAVIMETRIC ANALYSIS

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ACADEMIC ABSTRACT

The purpose of this thesis is to examine the potential of a novel method for analysis and characterization of coal mine dust. Respirable dust has long been an industry concern due to the association of overexposure leading to the development occupational lung disease. Recent trends of increased incidence of occupational lung disease in miners, such as silicosis and Coal Workers Pneumoconiosis, has shown there is a need for a greater understanding of the respirable fraction of dust in underground coal mines. This study will examine the development of a comprehensive standard methodology for characterization of respirable dust via thermogravimetric analysis (TGA). This method was verified with laboratory-generated respirable dust samples analogous to those commonly observed in underground coal mines.

Results of this study demonstrate the ability of the novel TGA method to characterize dust efficiently and effectively. Analysis of the dust includes the determination of mass fractions of coal and non-coal, as well as mass fractions of coal, carbonate, and non-carbonate minerals for larger respirable dust samples. Characterization occurs through the removal of dust particulates from the filter and analysis with TGA, which continuously measures change in mass with specific temperature regions associated with chemical changes for specific types of dust particulates. Results obtained from the verification samples reveal that this method can provide powerful information that may help to increase the current understanding of the health risks linked with exposure to certain types of dust, specifically those found in underground coal mines.

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PUBLIC ABSTRACT

The purpose of this thesis is to examine the potential of a novel method for analysis and characterization of coal mine dust. Respirable dust has long been an industry concern due to the association of overexposure leading to the development occupational lung disease. Increases in lung disease over the past decade has shown there is a need for a greater understanding of the inhalable dust in underground coal mines. This study will examine the development of a standard method for characterization of inhalable dust found in coal mines. This method was tested with laboratory-generated dust samples similar to those commonly observed in underground coal mines.

Results of this study show the ability of the novel method to characterize dust efficiently and effectively. This method categorizes the dust into fractions of coal and non-coal, as well as fractions of coal, carbonate, and non-carbonate minerals for larger dust samples. Characterization occurs through removing particles of dust and subjecting them to thermogravimetric analysis (TGA). Using TGA, samples are heated in a controlled environment and the change in weight of the samples is monitored as they burn or break down in specific temperature ranges. Results obtained from the laboratory-generated samples reveal that this method can provide powerful information that may help to increase the current understanding of the health risks linked with exposure to certain types of dust, specifically those found in underground coal mines.

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Abstract

Respirable dust in underground coal mines has long been associated with occupational lung diseases, particularly coal workers' pneumoconiosis (CWP) and silicosis. Regular dust sampling is required for assessing occupational exposures, and compliance with federal regulations is determined on the basis of total respirable dust concentration and crystalline silica content by mass. In light of continued incidence of CWP amongst coal miners, additional information is needed to determine what role specific dust characteristics might play in health outcomes. While particle-level analysis is ideal, current time requirements and costs make this simply unfeasible for large numbers of samples. However, opportunities do exist for gleaning additional information from bulk analysis (i.e., beyond total mass and silica content) using relatively quick and inexpensive methods. Thermogravimetric analysis (TGA) may be a particularly attractive option. It involves precise sample weight measurement in a temperature controlled environment, such that weight changes over specific temperature ranges can be correlated to chemical changes of particular sample constituents. In principle, TGA offers the ability to determine the coal and total mineral mass fractions in respirable dust samples. Such analysis could conceivably be combined with standard methods currently used to measure total mass and silica content. Under some circumstances, TGA might also be extended to provide information on specific dust constituents of interest (such as calcite). In this paper, we consider the benefits and challenges of TGA of respirable coal mine dust samples, and provide preliminary results and observations from ongoing research on this topic.

Keywords: CWP, Occupational lung diseases, Thermogravimetic Analysis (TGA), Respirable dust, Silica.

1. Introduction

Over the past several decades, significant progress has been made toward improving worker health and safety at coal mining operations in the US (Suarthana et al., 2011;NIOSH, 1974;WHO,1999). However, respirable dust (i.e., particles less than about 5µm in aerodynamic diameter) is still a serious concern because exposures are associated with risks of occupational lung diseases, namely Coal Workers' Pneumoconiosis (CWP) and silicosis (USEPA, 2013). These diseases can severely decrease quality of life by limiting lung function, and in some cases may lead to progressive massive fibrosis (PMF), and can ultimately be fatal (USEPA, 2013; Castranova and Vallyathan, 2000).

While federal regulation along with a variety of technological and operational advancements have resulted in a significant decline of such diseases, incidence remains unacceptably high – particularly in parts of Central Appalachia (Laney and Attfield, 2010; CDC, 2006; dos Santao et al., 2005). In some areas of this region, there appears to even be an increase in the incidence of CWP and silicosis (Suarthana et al., 2011; Laney and Attfield, 2010; CDC, 2006; dos Santao et al., 2005). While the reason(s) for this has yet to be definitively determined, some explanations point to unique mining conditions in this region. Indeed, these mines employ a smaller workforce operating in thinner seams of coal (WHO,1999; Laney and Attfield, 2010; CDC, 2006; Schatzel, 2009). The reduced seam heights lead to mining of rock strata above and below the coal (i.e. the roof and floor), which may increase total dust exposures as well as exposures to specific types of particles based on their composition, size or shape. Moreover, the mining methods and mine sizes may also contribute to unique dust exposures. Continuous miners are generally employed with auxiliary support (e.g., roof bolting and shuttle car haulage), and most jobs have the potential for dust generation. Also, due to relatively small crews, many miners can perform a variety of jobs and thus work in a variety of conditions.

1.1. Current Sampling and Analysis Methods for Respirable Coal Mine Dusts

In May 2014, the Mine Safety and Health Administration (MSHA) released a new rule regarding respirable coal mine dust exposures (Federal Register, 2014). By August 2016, the permissible exposure limit (PEL) will be reduced from 2.0 to 1.5 mg/m^3 in production areas of mines; and from 1.0 to 0.5 mg/m^3 in entries used for ventilation and for "Part 90" miners (i.e., individuals already diagnosed with CWP). Moreover, in mines where respirable dust is comprised of greater than 5% quartz (by mass), the PEL is decreased to a mine-specific PEL in order to reduce health risks (see Ref) (Suarthana et al., 2011; Federal Register, 2014; 30 CFR Part 75). If a mine has silica content greater than 0.5 mg/m^3, extended cuts with a continuous miner (i.e. production cuts greater than 20 feet prior to roof bolting) are also prohibited. (30 CFR Part 75). To demonstrate compliance with the regulatory limits, personal dust monitoring is required for miners working in designated occupations which are identified by the increased risk for high dust exposure, such as the continuous miner or roof bolter operator (Federal Register, 2014; Colinet et al., 2010; Reed et al., 2008). Additionally, operators take samples in designated areas, including areas in the working face that are known for high dust generation for atmospheric concentrations and potential exposure for workers (Federal Register, 2014). The new dust rule requires that compliance monitoring now be conducted when production is at least 80% of full production levels (i.e., as opposed to the 50% threshold that was required previously) (Federal Register, 2014).

Presently, dust monitoring involves collecting a full-shift sample with a permissible pump (i.e., certified intrinsically safe), sampling tube, and Dorr-Oliver cyclone (nylon, cut point of ~4 µm). Samples are collected onto polyvinyl chloride (PVC) filters of known weight housed in pre-assembled cassettes (Colinet et al., 2010; Zefon, 2015). The pump is run at a flow rate of 1.7 L/min to mimic the rate of human respiration (Colinet et al., 2010; Zefon, 2015); it is turned on when the miner enters the mine and left running until the miner returns to the surface. The sample is then shipped to a certified lab for analysis.

Analysis of respirable dust samples currently includes two results: the total sample weight, which can be converted to a mass concentration of exposure (mg/m^3), and the mass fraction of crystalline silica in the sample. The sample weight is determined gravimetrically (i.e., by difference between the filter weight before and after sample collection) (Colinet et al., 2010; Zefon, 2015; Bartley and Feldman, 1998), and the silica fraction is determined by infrared spectroscopy (IR) by either NIOSH Method 7603 or MSHA Method P7 (Schlecht and Key-Schwartz, 2003; MSHA, 2014). For both methods, the PVC filters are ashed to remove organic matter (i.e. coal dust and the filter) and unoxidized material is redeposited on a vinyl acrylic copolymer filter, which can be scanned with IR (Schlecht and Key-Schwartz, 2003; MSHA, 2014)..

As of February 1, 2016, compliance monitoring will also include use of the continuous personal dust monitor (CPDM) for miners working in high-dust areas (Federal Register, 2014). The CPDM is a wearable unit that allows quasi real-time monitoring of total respirable dust exposures by measuring incremental changes in the weight of a filter as it collects dust over time. The idea is that miners can track their exposures during their work and make timely decisions to reduce their health risks. The CPDM does not allow for determination of silica content in respirable dust, and so silica must still be measured on samples collected and analyzed as described above. In order to provide more timely information regarding silica exposures, NIOSH is currently researching methods for direct-on-filter analysis that could be used immediately following sample collection (i.e., end of shift) (Colinet et al., 2010; Reed et al., 2008; Sellaro, 2014; Tuchman, 1992; Tuchman et al., 2008). While an ultimate goal would be real-time measurement of silica, end-of-shift results would certainly be an improvement over current methods.

1.2. Needs for Expanded Analysis

The field is indeed advancing toward faster capabilities for quantifying respirable coal mine dust exposures by total concentration and silica content, the two focal points of current regulation. But many other exposure aspects may be useful in understanding health risks and effects, particularly in light of apparent differences in lung disease rates between various coal mining regions (Suarthana et al., 2011; Castranova and Vallyathan, 2000; CDC, 2006). Regarding the dust itself, characteristics such as particle shapes, sizes and chemistries may all be important. For instance, particle size and shape may play a role in the how well dust can penetrate and become embedded in lung tissue (Federal Register, 2014; Mischler, 2014), and a combination of size and chemistry may influence the relative reactivity of particles within the respiratory system (Mischler, 2014; NIOSH, 1991). Ideally, many individual particles could be analyzed to determine distributions of these characteristics. In reality, this is *possible* by methods such as scanning electron microscopy with energy-dispersive x-ray (SEM-EDX) – but far from *feasible* at large scale due to costs and time requirements (MSHA, 2014). However, there is potential to gather more data from dust samples than is currently done, without having to examine individual particles.

An objective of ongoing research by the authors is to develop efficient and relatively inexpensive methods for expanded analysis of respirable coal mine dust samples. Currently, we are focused on opportunities for using thermogravimetric analysis (TGA).

2. *Thermogravimetric Analysis*

TGA is used to monitor weight change of a sample as it is exposed to changing temperature in a given atmosphere (Coats and Redfern, 1963). Weight change is generally plotted as a function of temperature or time on a thermogram (Coats and Redfern, 1963; TA Instruments, 2006), and this information can be interpreted to understand chemical changes in the sample as it is heated. In some cases, TGA can be combined with additional analyses (e.g., to characterize the volatiles or reaction products that are generated as a sample decomposes) (Coats and Redfern, 1963; Cheng et al., 2010; Mu and Perlmutter, 1981; Hills, 1968; Gabor et al., 1995). In the context of coal, TGA has long been used to conduct proximate analysis, in which the goal is to determine the ash content of the coal (i.e., the non-combustible mineral fraction) (ASTM, 1994; Mayoral et al., 2001; Li et al., 2009). TGA has also been used for rank classification of coal samples (Mayoral et al., 2001).

The TGA instrument is comprised of two key components: the furnace and the balance. With tight control over the furnace chamber conditions (i.e., temperature and atmosphere) and a highly sensitive balance, experiments can be conducted with very good precision – for instance, allowing measurements of weight changes on the order of just a few μg. This ability has allowed proximate coal analysis to be done on very small sample sizes (ASTM, 1994; Mayoral et al., 2001). It also potentially provides an option for analysis of respirable dust samples from coal mines, which are typically on the order of tens to hundreds of μg.

2.1. Considering TGA for Respirable Dust Samples

At present, we are investigating the efficacy of TGA to estimate the mass fractions of coal (i.e., organic) and mineral (i.e., inorganic) content in respirable dust samples. For a very basic estimate, TGA of dust samples can be treated as analogous to proximate analysis of bulk coal samples: The coal content is oxidizable, and so is assumed to totally degrade (i.e., lose all of its mass) during the TGA process; whereas the mineral content does not appreciably degrade or react, and so the remaining residue at the end of the TGA experiment is taken as the total mineral mass. Figure 1.1 illustrates hypothetical thermograms for this general example.

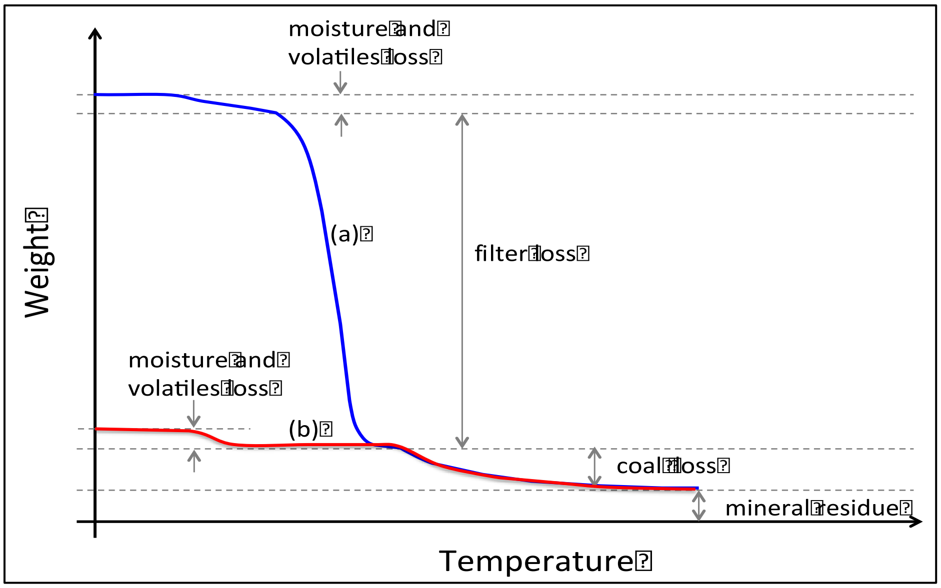

Figure 1.1. Hypothetical thermograms for (a) direct-on-filter and (b) dust only TGA of a respirable coal mine dust sample. For the direct-on-filter conceptualization, the filter media is assumed to decompose completely prior to coal oxidation.

In reality, the inorganic matter in a dust sample from a coal mine may include a number of different minerals from different sources. Minerals such as silica, silicates, or carbonates may be associated with shales or sandstones that make up roof or floor rock; and minerals such as pyrite or chloride salts may be ingrained in the coal seam. Of these, only carbonates are expected to react significantly within the same temperature range as coal. Carbonates can thermally decompose to mineral oxides and carbon dioxide, with the conversion of calcite ($CaCO_3$) to calcium oxide and carbon dioxide ($CaO + CO_2$) being a common example (Sellaro, 2014; Cheng et al., 2010; Mu and Perlmutter, 1981; Hills, 1968; Gabor et al., 1995). Thus, a more accurate estimate of coal and mineral fractions within a dust sample by TGA might necessitate separation of coal oxidation from carbonate decomposition.

The issue of carbonate content in coal mine dust samples is further complicated by “rock dusting” activities. Rock dust is primarily composed of calcite and/or dolomite ($CaMg(CO_3)_2$), and dusting is required in certain areas of mines to prevent propagation of coal dust explosions (30 CFR Part 75). In areas with heavy rock dust applications, or when the rock dust product has a high proportion of very fine particles, rock dust might contribute significantly to the total respirable dust concentration (30 CFR Part 75). TGA of samples from such areas should therefore consider calcite and/or dolomite, specifically; otherwise a simple proximate analysis approach as described above may overestimate the coal dust fraction.

The potential for using TGA to specifically estimate rock dust mass in a sample may also be of interest because it could allow operators to understand the influence of their rock dusting programs on respirable dust concentrations in the mine environment. As dust exposure limits are reduced with new regulation, understanding which activities are contributing dust is critical for compliance efforts. While the main components of rock dust are not generally considered to adversely affect lung health, regulatory dust limits are currently aimed at total dust concentration (and silica mass content) – and so even innocuous dust particles are concerning.

3. *Development of a TGA Method for Respirable Coal Mine Dust Samples*

In principle, TGA of coal mine dust samples could be done as an intermediate step between current standard methods for assessing the total weight of a sample and its mass fraction of silica (i.e., NIOSH 7603 or MSHA P7) (Schlecht and Key-Schwartz, 2003; MSHA, 2014).. As illustrated in Figure 1.1, TGA might be done directly on the filter used to collect the dust sample, or on dust that has been removed from a filter. In either case, due to very small sample masses, a very sensitive TGA instrument is required.

For development of TGA method for respirable coal mine dust samples, we are using a Q500 Thermogravimetric Analyzer (TA Instruments, New Castle, DE). The Q500 employs a microbalance with 0.1μg resolution, and its vertical furnace eliminates some thermal influence on the balance (Cheng et al., 2010; Colinet and Listak, 2012). The instrument is highly programmable, such that users can create precise methods that may be run without interference. Our instrument is also equipped with an autosampler, which provides the ability to run up to 16 separate samples in sequence. Platinum sample pans are used due to their inertness across a wide temperature range and because they are easy to clean.

To date, our method development work has focused on both direct-on-filter and dust-only TGA of respirable coal mine dust samples.

3.1. Direct-on-filter TGA

For a direct-on-filter method, the idea is simply to "ash" the entire sample filter in the TGA instrument. As such, an understanding of the filter media behavior as it is heated, and any potential interactions between it and the sample matrix, is needed. Ideally, the filter media: decomposes in a separate temperature range from the sample matrix; is highly uniform with respect to its ash content; and can be folded to fit in the TGA pans without significant mass loss. Considering the relative weight of filters (i.e., tens of mg) versus a typical dust sample (i.e., tens to hundreds of µg), decomposition of the filter at a different temperature than the coal (and other sample components such as calcite) is particularly important. Moreover, compatibility of the filter media with current dust sampling and analysis protocols should be considered.

Thus far, two filter media types have been evaluated: PVC and MCE (mixed cellulose ester). Both filter types are available in the 37 mm size commonly used for dust sample collection in underground coal mines, and both can be used for respirable dust sampling, specifically (Danley and Schaefer, 2008; Zefon, 2012 and 2015). Table 1.1 provides a comparison of key characteristics, with favorable characteristics denoted by a star.

Table 1.1. Comparison of PVC and MCE filter media characteristics

PVC	MCE
★Non-hygroscopic	Hygroscopic
Static charging possible	★Low static charging
Some ash content	★Virtually ashless
★Pliable	Tears easily

PVC is currently used for respirable dust sampling in coal mines, and so is favorable from the perspective of utilizing TGA as an intermediate step between current gravimetric (i.e., total dust sample weight) and silica content analyses. However, PVC filters generally have ash content, which could complicate determination of mineral content in the dust sample matrix; and they also are subject to static charging issues (Zefon, 2015). MCE, on the other hand, is considered ashless and not susceptible to static buildup (Zefon, 2012). But the material is relatively hygroscopic, meaning it can easily absorb moisture, and this is problematic from the standpoint of current gravimetric analysis (i.e., accurately determining the dust sample weight is difficult) (Zefon, 2012).

3.1.1. Summary of Experiments and Results

To test the suitability of PVC and MCE filters (37 mm, 5µm pore size) for direct-on-filter TGA of respirable coal mine dust samples, preliminary experiments were conducted (see Keles et al., 2015, for more details). Blank filters of each type (n=20) were ashed under a variety of conditions to observe their behavior; and several samples of pulverized raw coal (with varying mineral content) have also been ashed to simulate a dust sample that might be collected underground. Figure 1.2 shows typical thermograms for PVC, MCE and coal dust TGA experiments conducted in air (i.e., oxidizing environment). The main observations from these experiments were:

- Coal oxidation occurs above about 425°C; at lower temperatures, some moisture and volatiles are also lost.
- PVC filters weight between about 15-18mg. They decompose in two primary stages (i.e., around 285°C, and then above about 450°C); the latter stage overlaps significantly with coal oxidation. The weight change ratio between these two stages of decomposition is not reproducible enough to predict the weight change in the coal oxidation region with sufficient accuracy. Ash in PVC filters tested is highly reproducible and accounts for about 0.13 ± 0.02% of total filter weight. Static charging was not observed to be a significant issue.
- MCE filters weigh between about 35-37mg. They decompose primarily below 425°C (i.e., losing about 98.5% of their weight), and the weight change ratio between decomposition before 425°C and after is highly reproducible. MCE ash content is also highly reproducible, and accounts for about 0.03 ± 0.01% of the total filter weight. Filter pliability can be increased misting the filters with high purity water during folding.

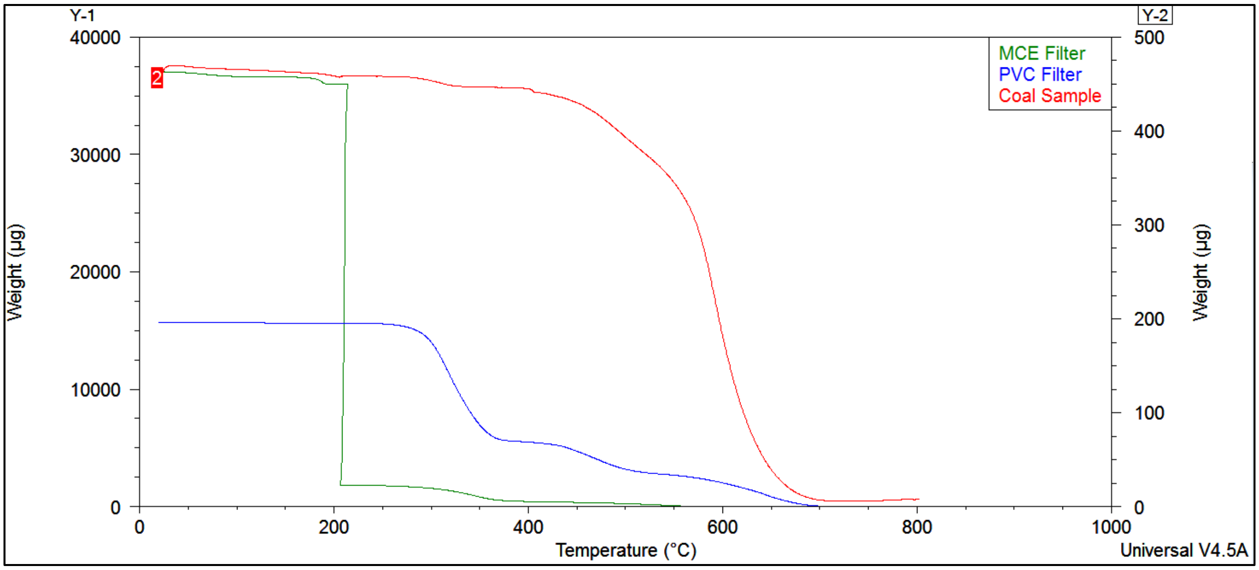

Figure 1.2. Example thermograms for blank PVC and MCE filters (primary y-axis) and a raw coal sample (secondary y-axis). The PVC filter has two regions of weight loss, which span relatively wide temperature ranges, whereas the MCE filter loses most of its weight in one very narrow region. Coal oxidation is significant at temperatures above about 425 °C.

For the MCE filters, pre- and post-weighing the filter may not provide an accurate sample weight due to moisture uptake, so the idea was to interpret the TGA results to determine the dry sample weight (i.e., by using the known filter decomposition rate and ash content as previously determined

For the dust on PVC filters, the coal and mineral fractions could be determined with good accuracy (i.e., as compared to the known ash content of the coal sample used to generate the dust). The coal and mineral fractions were determined using a simple proximate analysis approach: the dust sample weight was found as the difference between pre- and post-collection filter weight; the dust mineral weight was found as the difference between the final residue weight and the known ash content of the filter; and the dust coal weight was found as the difference between the dust sample weight and the dust mineral weight. Such analysis could certainly be conducted between current gravimetric and silica analyses for respirable dust samples; indeed, a sensitive TGA is not even needed for this, only the furnace and appropriate microbalance that are already used. However, this approach does not allow for determination of specific mineral components (e.g., calcite) of a dust sample.

Despite promising results from experiments on raw coal material and MCE separately, results from TGA of dust on these filters proved that direct-on-filter analysis is likely not possible. Figure 1.3 illustrates the reason for this. When the MCE begins to decompose just below 200°C, it appears that the coal particles immediately oxidize as well. As can be seen in the figure, the weight loss around this temperature associated with the dust-laden filter accounts for more than the filter weight; it also accounts for loss of most of the dust itself. This result was not initially expected, since in coal material-only experiments the primary weight loss did not occur until temperatures above 425°C. However, the result makes sense when considering that, although the furnace chamber temperature may only be around 200°C when the MCE filter decomposes, the local temperature where this reaction is happening should be much greater, and thus triggered spontaneous combustion of the coal particles. Considering the very fine size of the particles, and hence their large surface area, this result is not so surprising in retrospect. This explanation is supported by the small spike in furnace chamber temperature that can be seen Figure 1.3.

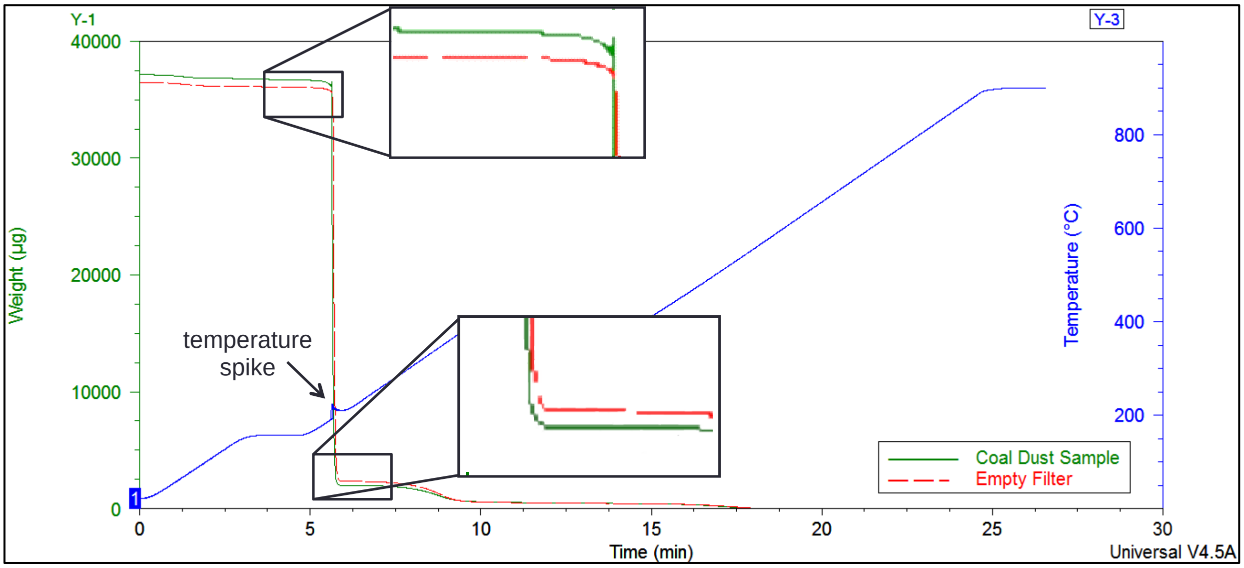

Figure 1.3 Thermograms (weight on the primary y-axis vs. time) for a blank MCE filter and an MCE filter with dust generated from a raw coal sample; temperature is shown on the secondary y-axis. The difference in initial weights is about 80µg, with the dust-laden filter being heavier than the empty filter; the difference in filter weights after the significant decomposition just above 200°C is about 30µg, with the dust-laden filter now being lighter than the empty filter. This result indicates that the coal dust spontaneously combusted when the MCE filter

decomposed. The furnace chamber temperature spike indicates that the MCE decomposition did indeed create significant heat.

In summary, direct-on-filter TGA using PVC filters is possible, but will not likely yield results that provide insights beyond a basic ratio of oxidizable to nonoxidizable content in a dust sample. Direct-on-filter TGA using MCE does not appear favorable at all, since the hygroscopic nature of the filters makes dust sample weight difficult to determine directly, and sample decomposition cannot be distinguished from filter decomposition during the TGA procedure.

Moreover, if determination of rock dust content in respirable coal mine dust samples is important, the sample will likely need to be removed from filters prior to TGA. This is because, similar to the effect that MCE filter decomposition has on spontaneous coal oxidation at relatively low furnace temperatures, calcite and dolomite may thermally degrade earlier than expected when in contact with the MCE material. Alternatively, an inert filter across the temperature range required to completely oxidize coal particles (e.g., glass fiber) might provide an option for direct-on-filter TGA with the opportunity to estimate rock dust content. However, this option could not be easily integrated between the current standard methods for gravimetric and silica content analyses.

3.2. Dust-only TGA

To increase resolution of TGA results and allow for evaluation of specific components of a respirable coal mine dust sample, particles may be removed from the filter on which they were collected. In principle, dust removal can be done on any filter – including perhaps the small glass fiber filters that are used in CPDMs. A procedure similar to that described in the sample preparation sections of the NIOSH 7603 or MSHA P7 can be used; in these methods, it is necessary to remove the silica-containing residue from a secondary filter following ashing of the PVC sample collection filter. In short, the filter is submersed in a tube of isopropanol, which is then briefly placed in an ultrasonic bath (or sonicator). The ultrasonic energy shakes the dust particles from the filter, which can then be removed from the tube, and the isopropanol is then evaporated. The residue in the tube then contains the dust particles. A fundamental assumption for a dust-only TGA method will of course be that the dust removed from the filter is representative of the entire sample on the filter.

3.2.1. Preliminary Observations Regarding Feasibility of Dust Removal

Preliminary experiments are underway to investigate the feasibility of removing respirable dust from PVC and MCE filters (37 mm, 5µm pore size) that are compatible with approved dust sampling pumps for underground coal mines, and also the glass fiber filters that are specifically manufactured for use with the CPDM. Based on the interference between filter decomposition and coal dust oxidation observed during direct-on-filter TGA experiments, one major goal of the current work is to determine how to maximize dust particle removal while minimizing filter degradation that results in filter media particles being present in the removed dust sample.

To date, several important observations have been made regarding MCE and PVC filters:

- Isopropanol is not an appropriate medium for conducting the ultrasonic dust removal. In both cases, the filter media react with the isopropanol. Testing is ongoing with deionized water, which appears promising.
- For blank filters, sonication times of 0.5-3.0 minutes appear to have similar effects on filter degradation, meaning that similar amounts of filter residue result from these times. The residue is on the order of tens of µg, which should dramatically reduce the tendency for filter decomposition to spur dust decomposition during TGA of removed dust samples. Sonication for longer periods of time results in the filters breaking down significantly, and thus a significant mass of filter residue may end up in dust samples removed from the filters.
- TGA of residue from sonication of blank filters shows similar results to TGA of the blank filters themselves. This indicates that filter particles present in removed dust samples should behave similarly
- Significant dust can be removed from filters. At present, it appears dust removal from the CPDM filters is more efficient than from PVC and MCE filters. This is likely due to the smaller surface area of the CPDM filters (i.e., 14 mm in diameter), which allows a thicker layer of dust to accumulate vs. the 37 mm filters.

While TGA experiments on dust removed from filters has not yet been completed, the above observations provide some promise that a method can be developed.

3.2.2. Determination of Rock Dust Fraction

Experiments are also underway to evaluate the feasibility of determining the rock dust fraction of a respirable dust sample collected in a coal mine. To date, reagent grade calcite and a real rock dust sample (raw limestone with calcite as the major fraction and dolomite as a minor fraction) have been investigated. A TGA method has been developed which appears capable of distinguishing calcite and likely dolomite from coal dust

Figure 1.4 provides example thermograms of calcite, raw limestone and coal dust separately (top), and samples containing both the raw limestone and coal dust (bottom). The coal dust was generated from a raw coal sample as in other previous tests. The TGA method requires precise control over the furnace chamber. As noted in the figure, there are four primary phases of sample weight change during the method.

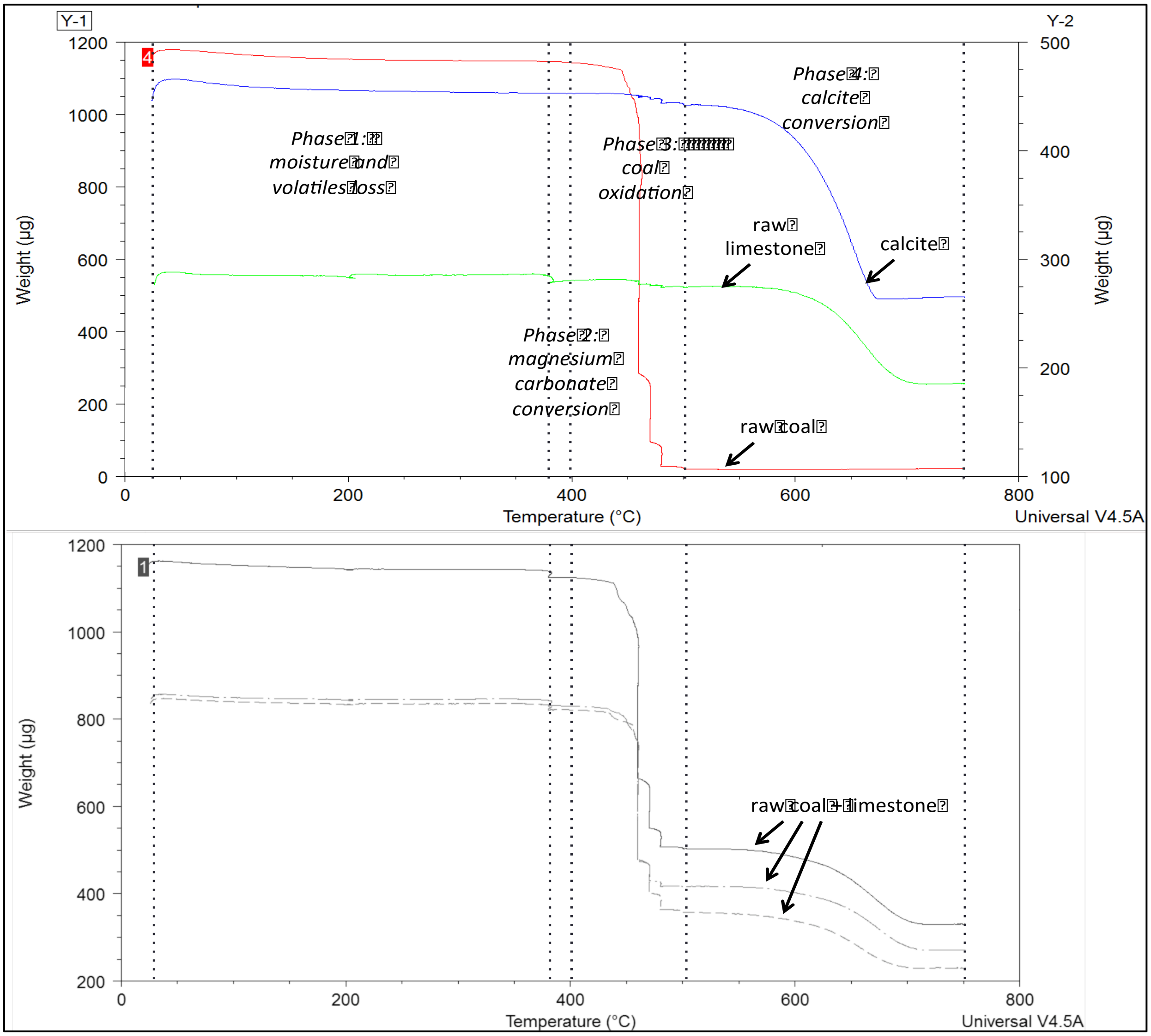

Figure 1.4 Example thermograms for reagent grade calcite only, raw limestone only and raw coal dust only (top), and samples containing both raw coal and raw limestone dust (bottom). The TGA experiment method used here includes four major phases, which drive off moisture and volatiles at temperatures less than about 380°C, convert a minor fraction of the limestone to an oxide between about 380 and 400°C oxidize coal particles between about 400 and 500°C, and convert calcite to calcium oxide between about 500 and 750°C. The residue at the end of the experiments represents calcium oxide and/or inert mineral content in the raw coal.

During the first phase of the TGA method only moisture and the small amount of volatiles from the coal are lost as the sample is heated to about 380°C. In the next phase, presumably the magnesium carbonate portion of the dolomite mineral lattice is converted to an oxide between about 380 and 400°C. In the third phase, the coal is oxidized as the temperature is ramped to about 500°C, and then the chamber is held isothermal for a relatively long period of time to ensure that coal oxidation is complete. The weight change in this phase is thus estimated to be the dry pure coal weight (i.e., non-volatile portion of the coal dust). In the final phase, the calcite is converted to calcium oxide as temperature is ramped to about 750°C, and held isothermal for some time again.

The residue (i.e., final weight) at the end of the experiment can be attributed to the calcium oxide and other mineral matter in the coal dust. Taking the weight change of the sample in the in the second and fourth phases of the method as the weight of carbon dioxide released during magnesium carbonate and calcite conversion, a stoichiometric relationship can be used to estimate the weight of these constituents in the sample, and also the weight of their resulting oxides. Finally, the difference between the experiment residue and the estimated oxide weights can be used to estimate the non-carbonate (i.e., inert) mineral weight in the coal.

As described, the developed method and determination of dust sample components (i.e., coal, carbonates, and all other mineral matter) does assume that rock dust is comprised completely of carbonates– which is not a practical assumption in many cases. However, the method and calculations can easily be adjusted based on more accurate assumptions. We are currently developing a modified TGA method to allow for determination of magnesium carbonate, which is associated with rock dust products containing significant dolomite. And since rock dust products are often assayed to determine fractions of calcite, dolomite and minor minerals, such information can be used to come up with mine-specific calculations. Regardless, the fundamental TGA work appears very promising in this area.

4. Conclusions and Future Work

There are undoubtedly needs for enhanced understanding of respirable dust characteristics in coal mines. TGA provides great potential for very simple determination of coal to total mineral ratios – analogous to proximate analysis of bulk coal samples. Such information could help provide insights into the sources of respirable dusts, and allow an additional basis of comparison between dusts from different mines, different areas of the same mine, or generated under different conditions. As well, TGA may provide opportunities to estimate more specific mass fractions of dust samples – such as the fraction associated with rock dust products.

The preliminary results and observations presented here reveal that direct-on-filter TGA of samples collected on PVC filter media may provide at least some information about coal vs. mineral fractions of respirable dust. Moreover, such analysis could be easily integrated into current standard methods for gravimetric and silica content analyses. For more accurate estimation of coal and mineral fractions, as well as the rock dust fraction specifically, dust-only TGA appears promising.

Continuing research is focused on optimizing the efficiency of dust removal from multiple filter types, and determining detection limits with regards to dust sample weights. Work is also needed to further develop the TGA method(s) appropriate for calcite and dolomite estimation. Complementary analyses to TGA methods for respirable coal mine dusts samples are additionally being considered, such as examining residue from TGA experiments with SEM-EDX to allow identification of specific mineral particles.

5. Acknowledgements

We extend our gratitude to the Alpha Foundation for the Improvement of Mine Safety and Health for funding this work. We thank Dr. Charles Potter from TA Instruments for his guidance with the development of a method using TGA. We also thank all mine personnel in Central and Northern Appalachian mines that have provided access and assistance to collect dust samples, and those that have shared their invaluable experience with our research team.

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Chapter 2. TGA Method for Estimating Coal, Carbonate, and Non-carbonate Mineral Mass Fractions in Respirable Mine Dust Samples

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Abstract

Incidence of occupational lung disease amongst coal miners in Central Appalachia has recently increased after decades of decline following the Coal Mine Health and Safety Act of 1969. The causes of this trend have yet to be fully explained – but particular dust characteristics may be a factor. Understanding more about respirable dust components requires analysis beyond what is currently done for demonstrating regulatory compliance. Thermogravimetric analysis (TGA) can provide estimates of coal and non-coal mass fractions of dust samples; and in some cases, the carbonate fraction and hence non-carbonate mineral fraction can also be determined. This paper presents the development and verification of a standard methodology for TGA of respirable coal mine dust samples, including sample preparation by removal of dust from MCE and PVC filter types via sonication. Data corrections related to the TGA instrument drift, sample preparation, and premature carbonate conversion are provided. The method is verified using laboratory-generated dust samples, with known coal, carbonate, and non-carbonate mineral mass fractions.

Keywords: Coal Mining, Thermogravimetric Analysis (TGA), Rock Dust, Respirable Dust, Occupational Lung Disease, CWP

1. Introduction

Respirable dust has long been recognized as an occupational health hazard for underground coal miners (Seixas et al., 1995). Chronic exposure can result in diseases such as black lung, commonly termed Coal Workers' Pneumoconiosis (CWP), or silicosis. Between about 1970-2000, regulatory measures coupled with improved technologies and operations management resulted in significant reduction in the incidence of such diseases amongst US coal miners (Suarthana et al., 2013; NIOSH, 1974; WHO, 1999). Between 2000-2010, however, an increase in CWP incidence was observed – with incidence rates particularly up central Appalachia (MSHA, 2008; Laney and Attfield, 2010; CDC, 2006; Antao et al., 2005).

While the cause for this trend is still not completely clear, changes in dust characteristics have been considered potential factors (e.g., see Pollock et al., 2010; Page and Organiscak, 2000; Bennett et al., 1979; Landen et al., 2011). For instance, mines in the central Appalachian region are tending to mine thinner seams of coal, and thus cut more roof or floor rock (Page and Organiscak, 2002; Laney and Attfield, 2010; CDC, 2006 and 2007; Schatzel, 2009), which may contribute relatively higher amounts of respirable dust constituents of concern (e.g., crystalline silica) (Pollack et al., 2010; Joy, 2012). Some correlation has indeed been shown between increased pneumoconiosis prevalence and increased mass concentrations of respirable silica in mines in this region (vs. other coal mining regions in the US) (Pollock et al., 2010; Joy, 2012) – but additional evidence is needed to draw hard conclusions. Moreover, it is possible that some combination of factors is at play, including those associated with both the dust itself (i.e., what types of particles are contained in the respirable fraction) and with an individual's exposure patterns (i.e., how frequently is an individual exposed to certain types of dust). It has been noted that central Appalachian mines are often relatively small in size and in personnel numbers (Antao et al., 2005; Laney and Attfield, 2010), which may translate to miners working in different production roles and hence different dust conditions relatively often (Antao et al., 2005; Joy, et al., 2010).

In an effort to lower risks of occupational lung disease for US coal miners, the Mine Safety and Health Administration (MSHA) has recently promulgated a new dust rule (effective August 2014). The rule tightens the limit on personal dust exposures from 2.0 to 1.5 mg/m^3 on the basis of time-weighted average (TWA) total mass concentration, and stipulates that TWA exposures are now calculated on the basis of an entire work shift rather than 8 hours as was previously the case from Title 30 of the Federal Code of Regulations (2014). It also requires implementation of continuous personal dust monitors (CPDMs) in order to allow miners to keep track of their exposure in (semi) real-time over their work shift, an increase in the frequency of compliance sampling by operators, and bases noncompliance findings on single samples (as opposed to an average of three samples) collected by MSHA (30 CFR Part 75).

At the same time that mine operators have been working to further reduce respirable dust and comply with new regulations, they have also been stepping up rock dusting programs (30

CFR Part 75; Fiscor, 2015). Rock dusting (i.e., coating the roof, ribs, and floor with inert dust such as limestone or dolomite) is required in underground coal mines in order to reduce risk of explosions, and rock dust products are specified on the basis of their particle size and composition. Fine particle size (i.e., less than 200 mesh or 75 μm) and inertness are key for ensuring that the dust functions as desired, and inclusion of crystalline silica must be limited due the respiratory health hazard it poses (30 CFR Part 75). Concerns over the possibility that some products may be out-of-spec for silica content (i.e., as measured on a mass basis) have recently been addressed by Colinet and Listek (2012). They found that, while over 90% of products tested contained less than 4% silica (free or crystalline), nearly 90% contained relatively high proportions of respirable sized dust (i.e., more than 20% of the total particles by volume (MSHA, 2015). With respect to respirable silica, Colinet and Listek concluded that the potential exists, if even remote, for rock dusting to contribute to exposures (2012). Though they did not specifically discuss the contribution of rock dust to the total amount of respirable dust in the mining environment, their results also suggest that this contribution may be sizable in some circumstances.

1.1. Analysis of Respirable Coal Mine Dust

At present, routine analysis of respirable dust samples from coal mines can yield two primary metrics: total mass concentration, which is determined gravimetrically, and silica mass fraction, which is determined by infrared absorption spectrophotometry (IR) using the MSHA P7 or NIOSH 7603 method (MSHA, 2014; Schlecht and Key-Schwartz, 2003). These metrics are used for assessing compliance with regulations. However, a more thorough understanding of dust characteristics is clearly needed to shed light on occupational health risks and outcomes, as well as the sources of specific dust constituents. While a variety of analytical techniques might be considered to study coal mine dust, relatively few are compatible with current sampling methods (i.e., collection of dust onto a standard gravimetric or CPDM filter) or requirements (i.e., use of intrinsically safe equipment underground).

Thermogravimetric analysis (TGA) is one technique that has potential to be applied to samples gathered using current protocols. TGA involves tracking the weight loss of a sample as it is heated. If specific components in the sample are known to thermally degrade/oxidize at particular temperatures, observations of weight loss can then be related to those components.

TGA is commonly used for proximate analysis of coal (see ASTM, 1994), which involves heating a sample to remove moisture and subsequently oxidize the organic matter (i.e., coal), and the remaining matter is attributed to ash-forming minerals. Likewise, for dust samples from underground coal mines, TGA can be used to estimate the total coal to total mineral mass fractions, including silica, silicates or other minerals that might be contained within the coal seam or cut from adjacent strata, as well as mineral matter associated with rock dusting activities. Preliminary work has indicated that TGA may allow estimation of the carbonate mass fraction, specifically (see Scaggs et al., 2015). In cases where rock dust products are known to have relatively low non-carbonate fractions and where additional carbonate sources are not prevalent, the carbonate mass fraction may serve as an acceptable surrogate for rock dust. Furthermore, because TGA can be performed after measurement of the total sample mass and determination of the silica fraction requires ashing of the sample anyway, a TGA method could be developed that simply fits between current analytical methods for respirable coal mine dust.

Prior work by the authors has focused on identifying critical factors for a successful TGA method and conducting preliminary experiments to observe behavior of expected dust components from coal mines, as well as filter media used for sampling (see Scaggs et al., 2015; Keles et al., 2015). That work has confirmed that the primary dust components of interest (i.e., coal, carbonate minerals, and all other minerals) can be discerned from TGA in an oxidizing atmosphere. Importantly, oxidation of coal and conversion of carbonate minerals to oxides occur in separate temperature regions. However, it was observed that interferences from filter media (PVC and MCE) are problematic for resolving weight losses associated with specific dust components, and so a direct-on-filter TGA method is not advisable. Rather a dust-only approach is needed.

Building upon that prior work, the current paper presents a methodology for preparing and analyzing respirable coal mine dust samples thermogravimetrically. The method results in estimations of coal, carbonate, and non-carbonate mineral mass fractions. Verification is presented using laboratory-generated respirable dust samples from pulverized raw coal, rock dust and shale materials.

2. Method Development

The following sections describe experimental procedures used to generate, prepare, and perform TGA on respirable dust samples representative of those that might be collected in coal mines.

2.1. Sample generation and preparation

Since TGA is an inherently destructive technique and method development often requires a large number of samples collected under controlled conditions, all dust samples used here were generated in the laboratory. To do this, a sealed enclosure was loaded with dust material, which could be made airborne by use of a small fan or compressed air pulses (Figure 2.1). Escort ELF dust pumps equipped with 10 mm Dorr-Oliver cyclones (i.e., same as those used for compliance sampling in coal mines) were used at a flowrate of 2.0 L/min to sample the respirable-sized particles onto a PVC or MCE filter (5 um pore size) inside a two-piece plastic cassette with filter support pad. At this flow rate, the cyclone cut point is at approximately 10µm. The target sample size was about 500-1,000µg; this was based on a median TWA dust exposure in central Appalachian mines of about 0.70mg/m^3 (Suarthana, et al., 2011), which should equate to just under 500µg of dust on 37mm filter for an 8-hour shift. Initial testing of the apparatus indicated that about 100-200µg of sample was collected on a filter for each minute that a pump was running for efficient sample gathering. Dust weights were determined using a microbalance (Sartorius MSE6.6S, Goettengin, Germany).

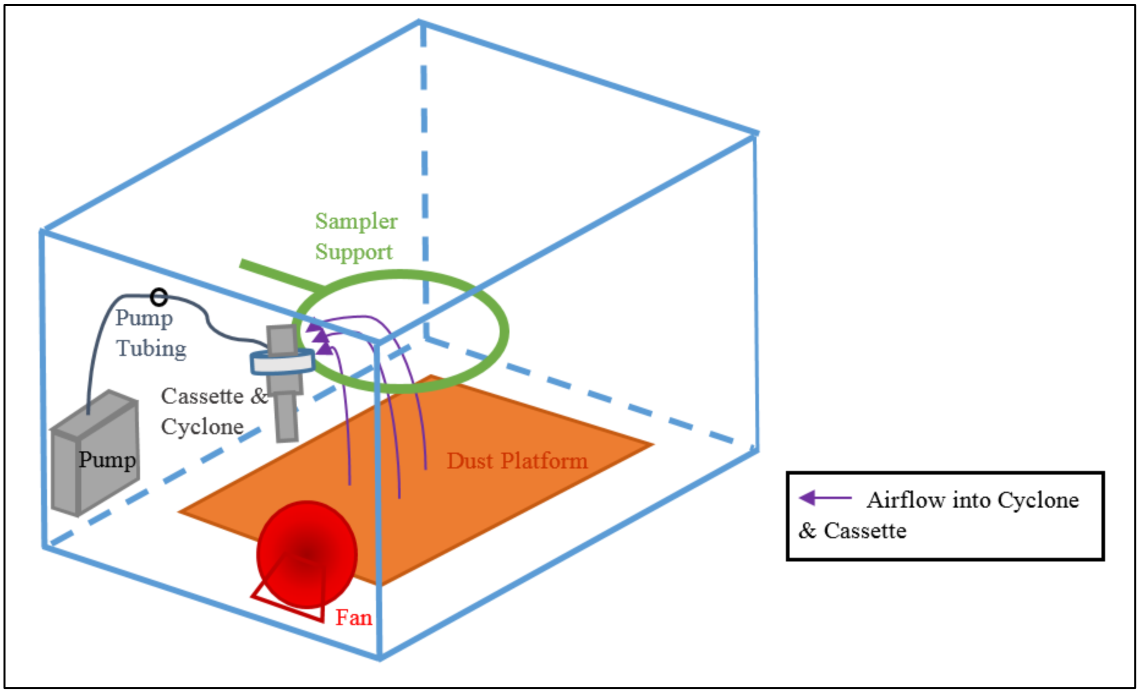

Figure 2.1. Schematic of laboratory set-up for respirable dust sample collection

The materials used to generate the respirable dust samples were pulverized raw coal, a real rock dust product, and pulverized shale pieces, which were handpicked from a large run-of-mine coal sample collected in central Appalachia (Peerless seam). Due to the fact that none of these are pure materials, it was expected that the coal would contain some small fraction of ash-forming minerals, the rock dust would contain some non-carbonate minerals, and the shale would have some coal content associated with it. For samples used during method development, only the coal and/or rock dust product was collected on each filter, and the total weight of dust collected was determined for all samples. For samples used to verify the method, all three materials were collected on a filter sequentially such that the weight of each material could be determined (i.e., filters were pre-weighed and then weighed after collection of each dust type).

As mentioned above, it is necessary to remove dust from the filters prior to TGA. To do this, filters were carefully removed from their cassettes using clean tweezers. Each filter was placed inside a clean 50 mL glass test tube (29 mm diameter). The size of the tube allows for a large enough circumference so that the filter can be slightly rolled, but its surfaces do not overlap obstructing dust removal. The tube was filled with approximately 25 mL of deionized (DI) water. Additional DI water was added to completely submerge the filter if needed. Test tubes were then placed in an ultrasonic bath (Cole-Parmer 08895-4, Vernon Hills, Illinois) and sonicated for 1 minute. During preliminary testing, this amount of time was sufficient to recover a significant dust mass, which will be discussed below, without removing excessive filter mass, which may interfere with TGA results. After sonication, the filters were carefully removed from tubes to minimize disturbance of any dust particles in the water. Finally, the test tubes were placed in an oven at 180ºC to evaporate the water, leaving any dust residue in the tube.

A volumetric pipette was used to add 200 µL (unless otherwise specified) of reagent grade isopropyl alcohol to each test tube, making an effort to rinse the sides and bottom of the tube to collect as much of the dust residue as possible. The suspension was then removed from the tube using the same pipette tip and deposited into a clean, tared TGA pan. Pans were cleaned prior to each use by exposing to an open flame from a butane torch for at least ten seconds. Pans were tared empty in the TGA instrument (TA Instruments Q500, New Castle, DE) and also weighed using the microbalance. The microbalance data served as a check for TGA instrument measurements. After the alcohol had evaporated (about 30 minutes), each pan was weighed again with the microbalance.

2.2. TGA Routine and Bulk Sample Analysis

Typically on the same day that dust samples were deposited into the TGA pans, they were run in the TGA using the routine outlined in Table 2.1. This routine is based on preliminary work by the authors to determine the temperature ranges over which the expected sample components are reactive. Representative thermograms for bulk samples of the pulverized raw coal, rock dust, and pulverized shale are shown in Figure 2.2. These samples contained relatively large particles placed directly into TGA pans rather than collected on dust filters. From these results, it appears that coal oxidation occurs between approximately 360-480°C with the current TGA routine. The weight loss in this region can be used to estimate the coal mass fraction of a sample. The final residue associated with the coal sample shown in Figure 2.2 is non-oxidizable mineral matter, which would be referred to as “ash” in proximate analysis of a bulk coal sample. Considering dust in the respirable size range, particles are expected to be highly liberated such that their mass reports to the correct category.

Table 2.1. Steps in TGA Routine

1.	Select gas 2, Air
2.	Ramp 50.00°C/min to 200.00°C
3.	Isothermal for 5.00 min
4.	Ramp 50.00°C/min to 380.00°C
5.	Isothermal for 5.00 min
6.	Ramp 100.00°C/min to 460.00°C
7.	Isothermal for 15.00 min
8.	Ramp 100.00°C/min to 470.00°C
9.	Isothermal for 5.00 min
10.	Ramp 50.00°C/min to 480.00°C
11.	Isothermal for 5.00 min
12.	Ramp 50.00°C/min to 500.00°C
13.	Isothermal for 1.00 min
14.	Ramp 50.00°C/min to 750.00°C
15.	Isothermal for 1.00 min
16.	Cool in gas 1, Nitrogen for 16 min

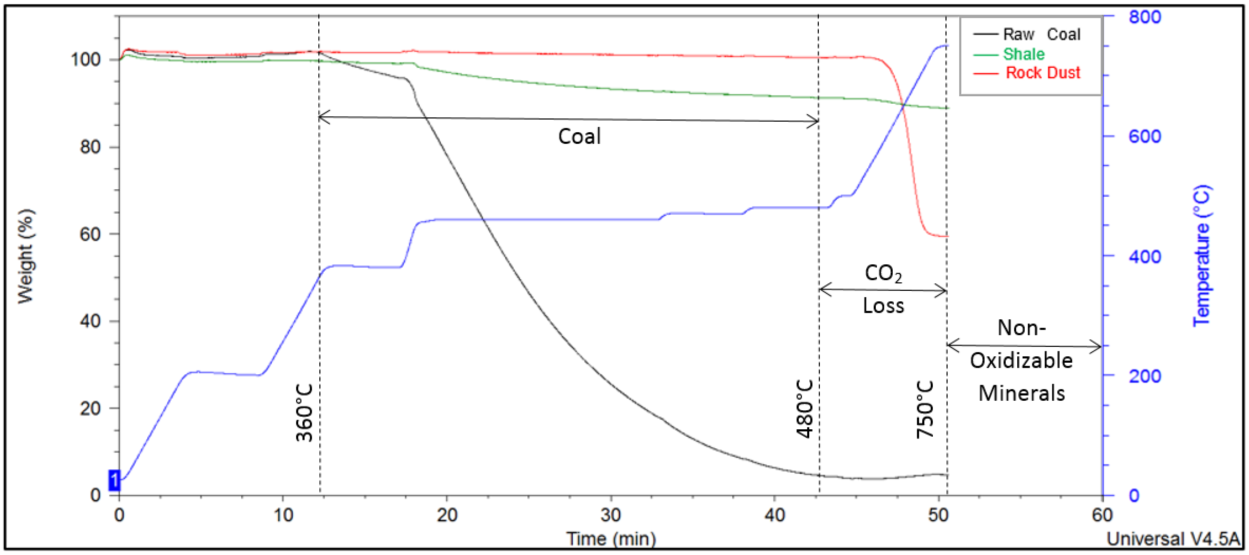

Figure 2.2. Representative thermograms for the raw coal, rock dust, and shale materials used to develop the TGA method

Also evident in Figure 2.2 is the behavior of carbonates in the rock dust sample, which do not begin conversion to oxides until about 480°C – after coal should be completely oxidized. The weight loss between 480°C and the end of the TGA routine can be attributed to carbon dioxide (CO_2) release, and accounts for about 40% of the total rock dust sample shown. From this weight loss, the carbonate mass fraction of a sample can be determined stoichiometrically by assuming specific carbonate minerals are present - i.e., the CO_2 molar mass fraction is 44% for pure calcite, $CaCO_3$, and 48% for dolomite, $MgCa(CO_3)_2$. The residue remaining at 750°C is attributed to the oxides produced from carbonate conversion, and any other non-oxidizable minerals contained in the rock dust. The non-oxidizable content of the rock dust used here was assumed to be 9% of its total mass, based on X-ray diffraction (XRD) analysis obtained for four different rock dust products used in the central Appalachian region (including some from the same producer as the sample used here). This showed that 91 ± 3% of the product mass is calcite or dolomite, with calcite accounting for roughly 75% of the total mass and dolomite accounting for roughly 17%. Based on the relative proportions of these two minerals from the XRD analysis, CO_2 was assumed to be 45% of the total carbonate mass – and resulting oxides were assumed to be 55%. Using these assumptions, TGA-derived mass fractions for the rock dust sample shown in Figure 2.2 are about 91% carbonate (40.5% CO2 and 50.5% oxides) and 9% non-oxidizable minerals – which are aligned with the XRD-derived fractions.

Finally from Figure 2.2, the shale thermogram indicates that this material is largely non-oxidizable – losing only about 10% of its weight. This loss is attributed primarily to impurity of the sample material used here, which likely contained some coal and some carbonate minerals. SEM-EDX data of the respirable sized shale material did confirm that it was primarily alumino-silicates, with some carbonaceous (i.e., coal) and carbonate particles.

Because the TGA routine takes over 50 minutes for each sample, the number of samples that can be run consecutively is limited (i.e., because nitrogen and/or air tanks must be replaced). All dust results reported here were obtained from TGA runs that included one empty pan at the beginning of the run, then six consecutive samples, and a final empty pan at the end of the run (i.e., eight total results); empty pan data is necessary for correcting sample results for internal drift of the TGA instrument. After the TGA run, all pans were weighed a final time using the microbalance, as a means of verifying the TGA data. TGA results were analyzed using the Thermal Advantage Universal Analysis software (also from TA Instruments), which allows detailed examination of weight loss and temperature profiles as well as user-defined macros for efficient extraction of specific data (e.g., weight loss values from multiple time ranges).

2.3. Corrections for instrument drift and sample preparation

Since respirable dust samples may have very small masses, it is necessary to correct TGA results for the internal drift of the instrument as well as influences of sample preparation. To establish a drift correction, which is specific to a given instrument and operating conditions, four sets of eight empty pans were run using the TGA routine in order to determine trends in weight change during single sample runs (i.e., from ambient to 750ºC) and over an entire sample set (i.e., from pan 1 to pan 8; see Table A.1 and Figure A.1 in Appendix A for summary of the data and thermograms). The total weight change during a run can be up to 21 µg, but the direction and magnitude of drift is reproducible within each temperature range of interest. An example of an empty pan thermogram is shown in Figure 2.3. Further, the initial pan weight can drift slightly from run to run within a set – but again the trend is reproducible. Taking the average weight results of each empty pan run (i.e, 1-8) and using the empty pan results in each sample set (i.e., 1 and 8), a correction can be applied to all dust sample results at every temperature of interest. Equation 2.1 shows the drift correction (C_{Drift}), where P_n is the average of the four nth pan weights from the empty pan run sets, and n represents the relative number of the sample pan (i.e., between 2 and 7) in the eight-pan sequence for a sample set; P_1 and P_8 are the average of the four pan 1 and pan 8 weights, respectively, from the empty pan run sets; and P_i and P_f are the weights for (empty) pans 1 and 8, respectively, from a given sample set.

$$\boldsymbol{C_{drift}} = \frac{-[(\boldsymbol{P_1}\text{-}\boldsymbol{P_n})*(\boldsymbol{P_i}-\boldsymbol{P_f})]}{(\mathrm{P_1}\text{-}\mathrm{P_8})} - \boldsymbol{P_i} \qquad \text{(Equation 2.1)}$$

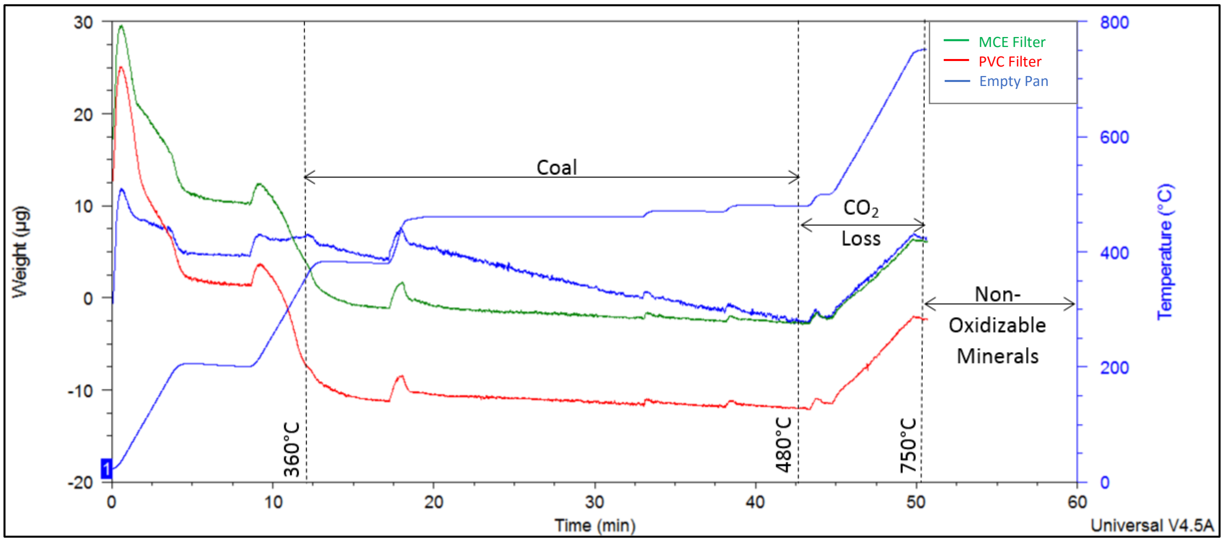

Figure 2.3. Representative thermograms for an empty pan and prepared blank PVC and MCE filters.

To determine the influence of the sample preparation on TGA results, 11 blank MCE and 13 blank PVC filters were tested. The blank filters were prepared identically to those on which dust samples were collected and then removed, except that clean sampling pumps were run in a fume hood (for 50-110 minutes) rather than in the dust collection enclosure (shown in Figures A.2 and A.3 in Appendix A). After sonicating the blank filters, evaporating the DI water, and removing residue with the isopropyl alcohol, the average residue deposited into the TGA pans was 35 ± 20 µg for PVC and 41± 27 µg for MCE. Using the TGA routine from Table 1, this residue lost virtually all of its weight before 480ºC (Figure 2.3). Furthermore, the weight loss ratio between ambient-360ºC and 360-480ºC was relatively high and repeatable (see Tables A.3 and A.4 in Appendix A for data and analysis) – allowing development of a sample preparation correction for each filter media that should be applied to the total sample and coal mass calculations.

A confidence interval of 95% is used to determine the lower and upper bands for the weight loss ratios of residue in the two temperature regions for MCE and PVC filters to minimize the risk of miscalculating the coal mass fraction. From ambient-360°C, 78.5% of the filter residue for MCE filters is lost with the remaining 21.5% of the residue is lost from 360-480°C while PVC filters experience a weight loss ratio of 66.5% to 33.5% for the same temperature regions, respectively. These values are used as constants in order to determine the corrections necessary for the calculation of the total sample weight and coal mass fraction based on the type of filter used for sample collection.

For the filter correction (C_{Filter}), any interference from the filter residue would occur in the temperature region associated with coal oxidation, 360-480°C. By determining the change in mass between ambient temperature ($M_{Amb.\ Temp.}$) and 360ºC ($M_{360^{\circ}C}$), and the weight loss ratios specific to the type of filter used for sample collection (i.e., WR is 78.5:21.5 for MCE and WR is 66.5:33.5 for PVC), the amount of filter residue present in the coal oxidation region may be estimated (Equation 2.2).

$$C_{Filter} = \left(\frac{M_{Amb.\ Temp.} - M_{360^{\circ}C}}{WR}\right) \qquad \text{(Equation 2.2)}$$

2.4. Preparation and TGA of respirable-sized coal and carbonate particles

In order to determine how respirable-sized particles of thermally reactive materials (i.e., coal and carbonate) behave during sample preparation and TGA, a series of lab-generated samples containing only coal, only rock dust, and coal and rock dust were prepared and analyzed. For PVC filters where total dust sample weight was recorded (n=12), 40 ± 22% of the dust was removed and deposited in the TGA pan for analysis. Figure 2.4 shows that, in general, dust recovery increases as total dust weight on the filter increases. Total dust weights were also recorded for MCE filters (n=12), but the accuracy of this data may vary due to the hygroscopic nature of the MCE media (i.e., moisture could have been lost or gained between measurement of initial and loaded filter weights). For comparison purposes, however, the dust recovery for MCE filters was estimated as 52 ± 20%.

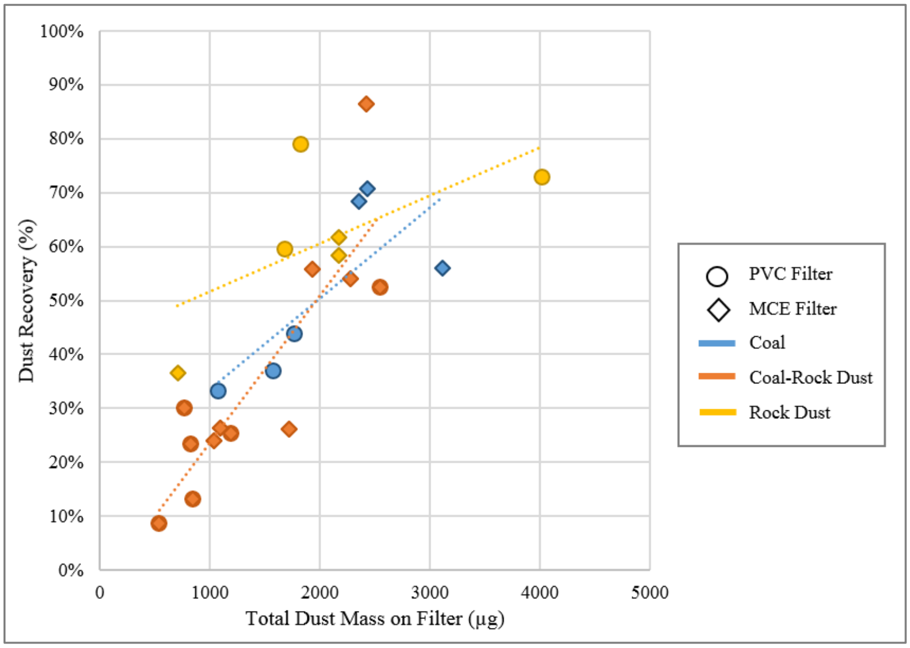

Figure 2.4. Dust recovery vs. total sample mass for lab-generated dust samples containing coal, rock dust, and coal and rock dust on PVC and MCE filters.

Figure 2.5 shows the TGA results of coal dust samples collected on PVC and MCE filters (results as weight percent are given in Figure A.4 in Appendix A). These confirm that the coal weight loss region for respirable dust samples analyzed with this particular routine should be taken as 360-480°C. Thus, total dust sample mass (M_{Dust}) and coal mass (M_C) can be calculated from Equations 2.3 and 2.4, respectively. $M_{360^{\circ}C}$, $M_{480^{\circ}C}$, and $M_{750^{\circ}C}$ refer to the recorded mass at each of these respective temperatures, and the appropriate constants for C_{Drift} should be chosen based on the filter type.

$$M_{Dust} = M_{360°C} - (C_{drift} + C_{filter}) \qquad \text{(Equation 2.3)}$$

$$M_{C} = (M_{360°C} - M_{480°C}) - (C_{drift} + C_{filter}) \qquad \text{(Equation 2.4)}$$

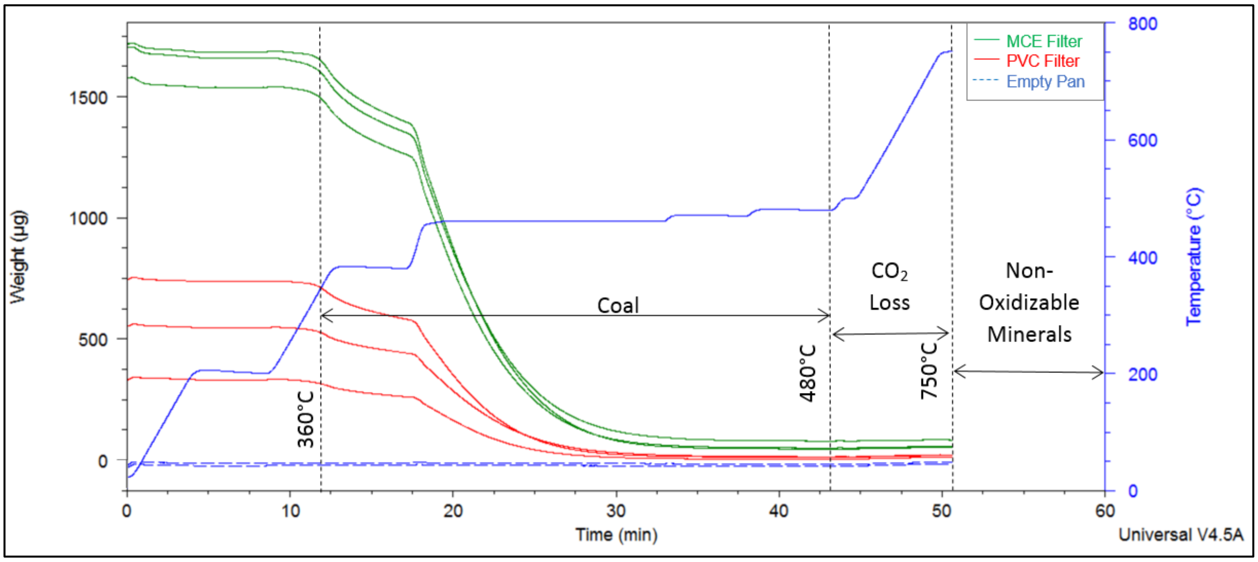

Figure 2.5. Thermograms from respirable coal dust samples collected in the lab on MCE and PVC filters.

It can also be seen from Figure 2.5 that the non-oxidizable or non-coal mass fraction of the respirable coal dust sample is similar to that of the bulk coal sample. This suggests that the sample preparation procedure does not bias results toward a particular dust component. Moreover, the fact that significant weight loss is not evident before about 360°C in these samples provides further confirmation that the preparation procedure does not tend to produce excessive residue. Based on Equation 2.2, less than 3 µg of weight loss in the coal region (i.e., 360-480°C) is attributed to the influence of sample preparation for any of these samples.

Figure 2.6 shows the TGA results for dust samples generated from rock dust on both filter types. It appears that these samples were slightly contaminated with coal particles (evident from the weight loss behavior that occurs in the coal oxidation region), which is likely due to collection of the samples in the dust enclosure following collection of coal dust. However, the results do confirm that significant weight loss occurs in the temperature range 480-750°C, signaling CO_2 release as carbonates are converted to oxides. This weight loss is simply termed the observed CO_2 mass ($M_{Obs.\ CO_2}$) (Equation 2.5).

$$M_{Obs.\,CO_2} = M_{480^\circ C} - M_{750^\circ C} \qquad \text{(Equation 2.5)}$$

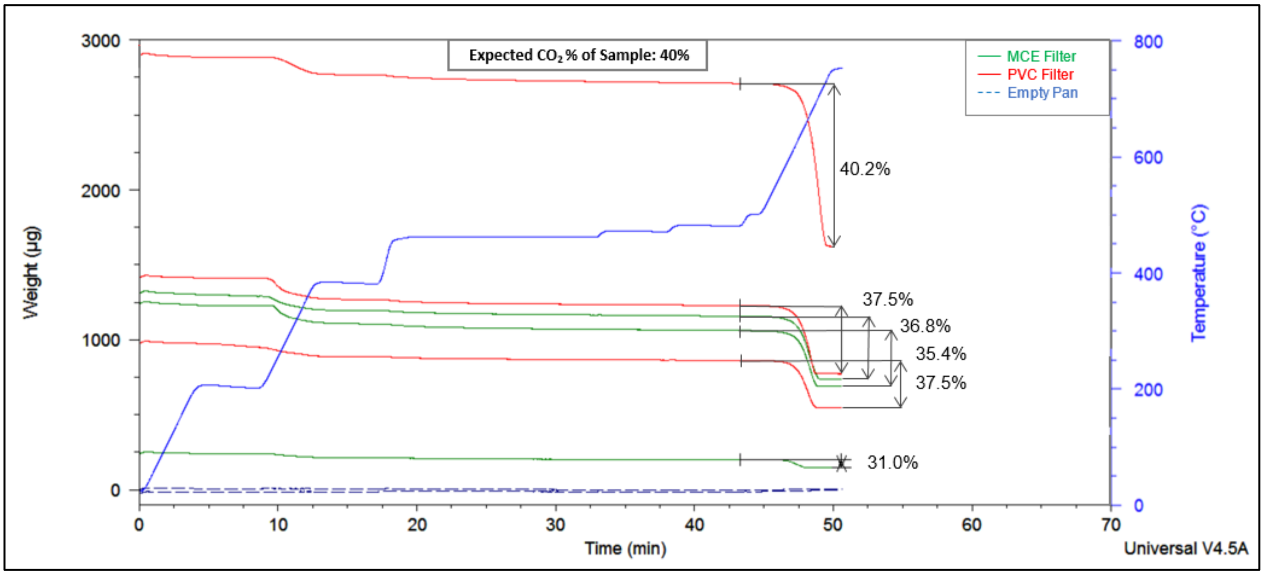

Figure 2.6. Thermograms from respirable rock dust samples collected in the lab on MCE and PVC filters. The weight loss between 480-750ºC are shown as a percentage of the sample weight at 480ºC.

Also from Figure 2.6, it appears that observed CO_2 weight loss is disproportionately correlated to the total sample size (i.e., smaller samples exhibit smaller CO_2 losses than expected). Based on the assumptions that the rock dust product tested contains approximately 91% carbonates by mass, which have a stoichiometric CO_2 content of 45%, the expected CO_2 weight loss should be about 40% of the weight value at 480°C. The trend in CO_2 weight loss with sample size suggests that some of the carbonates were converted to oxides prior to TGA analysis – probably during sample preparation, which has been previously been explored (Chou et al., 1989; Pokrovsky, et al., 2005; Plummer et al., 1978; Wollast, 1990). This trend was also observed for the samples containing both coal and rock dust (Figure 2.7).

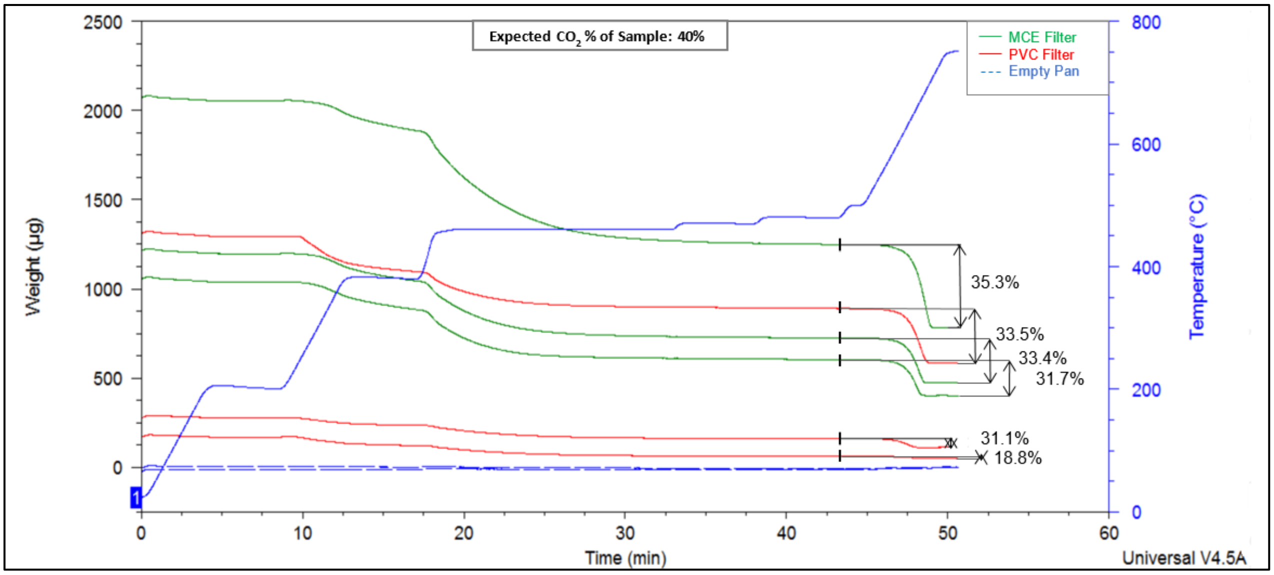

Figure 2.7. Thermograms from a mixture of respirable rock dust and coal dust samples collected in the lab on MCE and PVC filters. The weight loss between 480-750°C are shown as a percentage of the sample weight at 480°C.

Figure 2.8 shows the correlation between expected and observed carbonate mass for dust samples containing only rock dust and a mixture coal and rock dust (i.e., samples shown in Figures 2.6 and 2.7, respectively); the data fits well to a linear trend line. The observed carbonate mass, ($M_{Obs,\ Carb.}$), is stoichiometrically determined from the observed CO_2 mass (Equation 2.6). The expected carbonate mass, ($M_{Exp\ Carb.}$), is determined from the final residue (at 750ºC) that cannot be attributed to the non-oxidizable fractions of the coal or rock dust product (Equation 2.7). The residue associated with the non-oxidizable fractions is then classified as the non-carbonate mass ($M_{Non\text{-}Carb.}$) for the purposes of predicting the amount of other types of minerals (e.g. clays, shales, silica) which may be present in the respirable fraction. To predict mass of carbonates in a sample ($M_{Pre.\ Carb.}$) directly from the TGA data, Equation 2.8 gives the trend line shown in Figure 2.8 as a function of observed CO_2 mass.

$$M_{Obs.\ Carb.} = \frac{M_{Obs.\ CO_2}}{0.450} \qquad \text{(Equation 2.6)}$$

$$M_{Exp.\ Carb.} = \frac{(0.910 M_{750°C} - 0.056 M_C)}{0.450} \qquad \text{(Equation 2.7)}$$

$$M_{Pre.\ Carb.} = 1.042 M_{Obs.\ Carb.} + 64.483 \qquad \text{(Equation 2.8)}$$

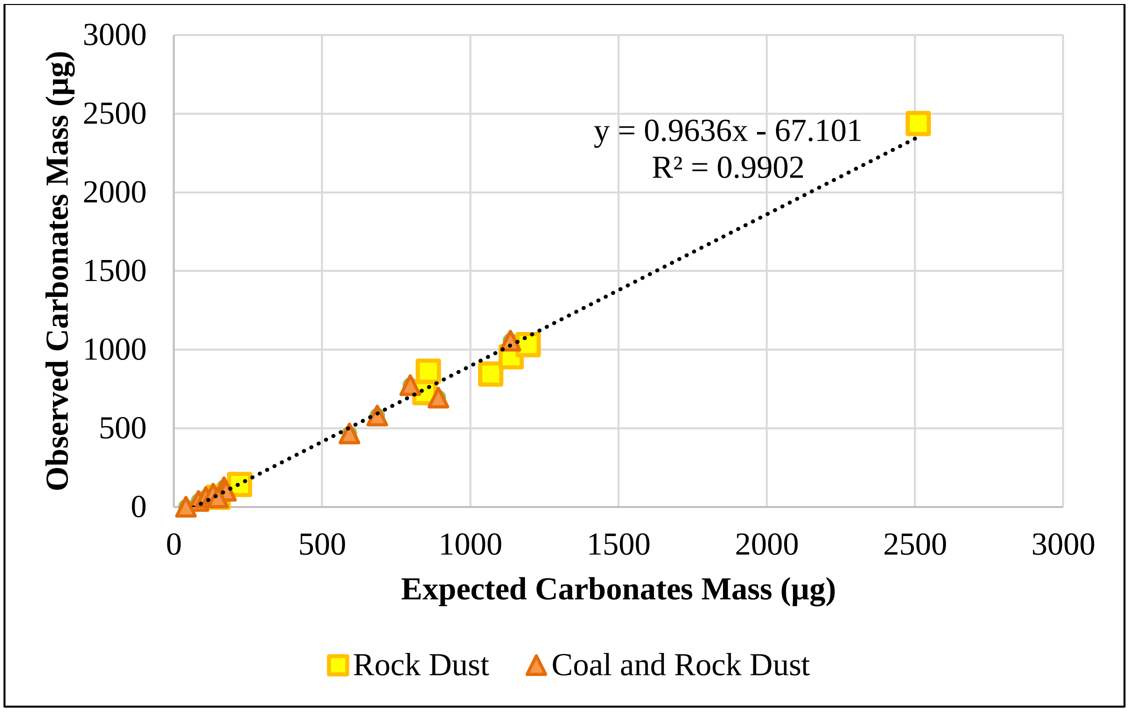

Figure 2.8. Calibration curve for observed versus expected carbonate mass in samples containing rock dust and coal and rock dust.

Figure 2.9 shows the ratio of observed to expected carbonate mass as a function of observed CO_2 weight loss. From Figures 2.8 and 2.9, the trends suggests that when the observed CO_2 weight loss is relatively small (i.e., less than about 30µg), error in the carbonate model prediction may be more significant. From this, the correction for carbonates here is applied to samples with greater than 30µg of CO_2 weight loss in order to contain the variability between predicted and expected carbonates mass fractions. With the CO_2 loss measured from the thermograms, it is possible to determine the minimum amount of carbonates present in the sample, however, this can lead to biasing in the non-carbonates mass fraction.

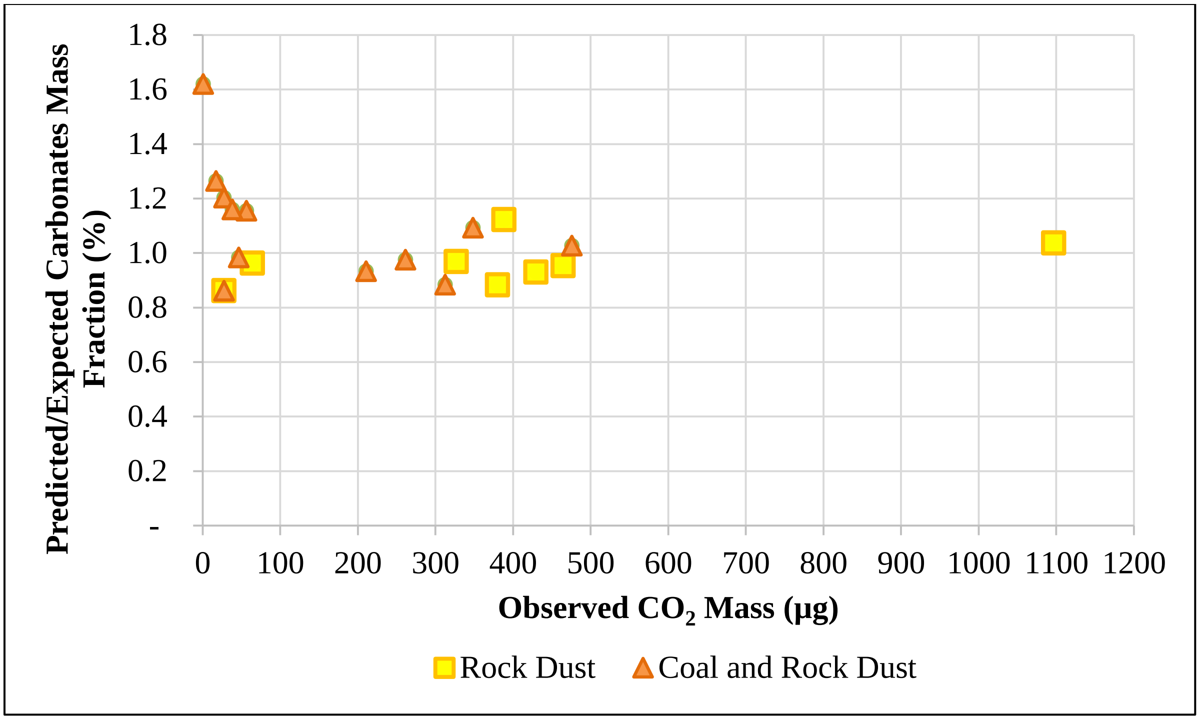

Figure 2.9. Ratio of predicted to expected carbonate mass versus observed CO_2 mass for samples containing rock dust and coal and rock dust.

Following determination of coal and (predicted) carbonate mass (Equations 2.4 and 2.8), the non-carbonate mineral mass ($M_{Pre.\ NO}$) can also be determined (Equation 2.9). It is the difference between the weight value at 480°C and the carbonate mass. Finally, the mass fractions of all dust components (i.e., coal, carbonates and non-carbonate minerals) can be estimated (Equations 2.10-2.12). It should be noted that, depending on the motivation for dust analysis and desired level of reporting, the carbonate and non-carbonate masses may be combined to determine a total mineral (i.e., non-coal) mass fraction ($X_{Non\text{-}Coal}$), especially with samples of small masses recovered to the TGA and low CO_2 weight loss.

$$M_{Pre.\ NO}=(M_{480\,°C} - M_{Pre.\ Carb.}) \qquad \text{(Equation 2.9)}$$

$$\textit{Coal Mass Fraction } (X_C) = \left(\frac{M_C}{M_{Dust}}\right) *100 \qquad \text{(Equation 2.10)}$$

$$\textit{Carbonates Mass Fraction } (X_{Carb.}) = \left(\frac{M_{Pre.\ Carb.}}{M_{Dust}}\right) *100 \qquad \text{(Equation 2.11)}$$

$$\textit{Non-carbonate Minerals Mass Fraction } (X_{Non\text{-}Carb}) = \left(\frac{M_{Pre.\ NO}}{M_{Dust}}\right) *100 \qquad \text{(Equation 2.12)}$$

3. Method Verification

For verification of the above method, a total of 43 composite samples were generated in the lab containing three materials (i.e., coal, rock dust and shale), collected in varying order. The weight of each material on the filter was determined gravimetrically during sample collection, and samples were prepared for TGA using the procedure previously described. Dust recovery is shown in Figure 2.10. Recovery again generally increased with total sample mass on the filter, and was higher for MCE than for PVC media. The sequence of dust collection was not observed to have any real impact on recovery. However, for 12 of the samples, up to 800 µL of isopropyl alcohol (i.e., as opposed to just 200 µL) was used to rinse dust from the test tubes into the TGA pans; and this did seem to increase recovery somewhat.

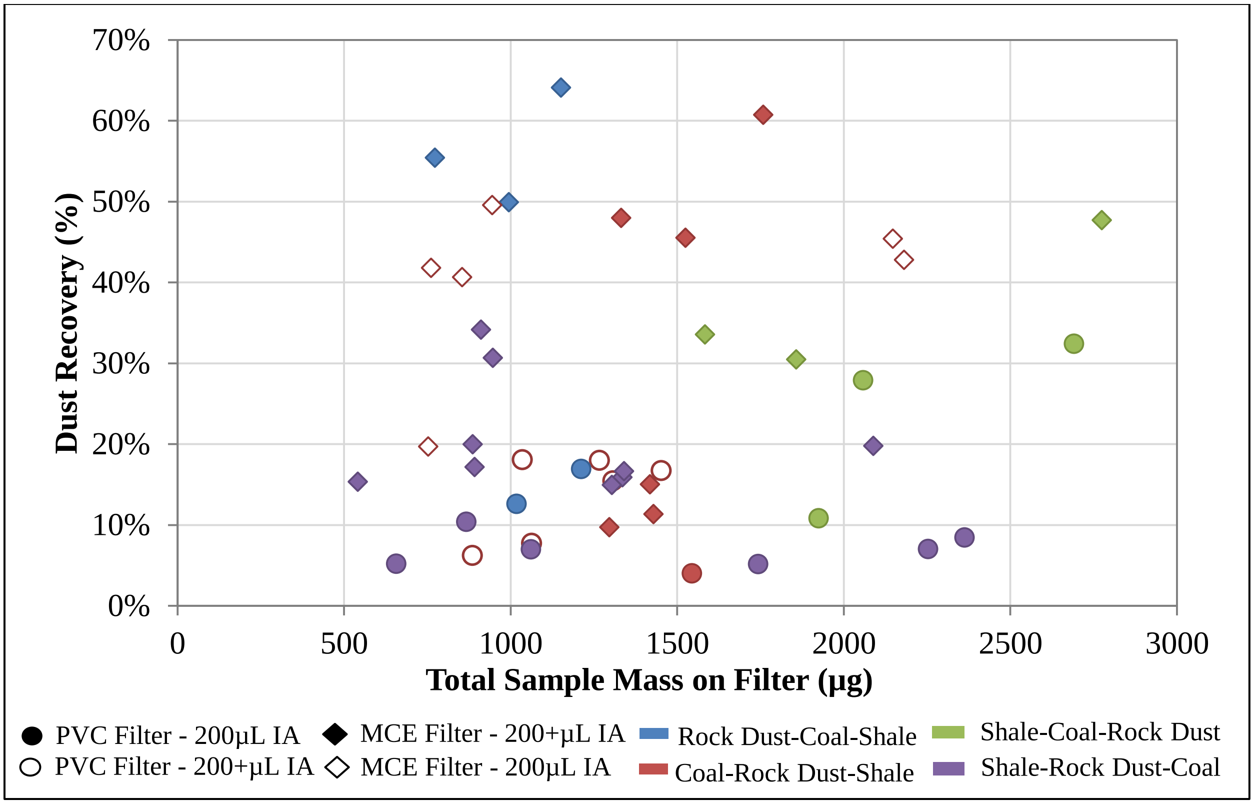

Figure 2.10. Dust recovery from filters shown by sequence of dust loaded onto the filter, filter type, and amount of isopropyl alcohol used for recovery of dust.

Several representative thermograms for the lab generated samples are shown in Figure 2.11 (all other data can be found in Appendix A in Figures A.5, A.6, A.7, and A.8). As expected, the two distinct regions of weight loss associated with coal oxidation and carbonate conversion were generally observed.

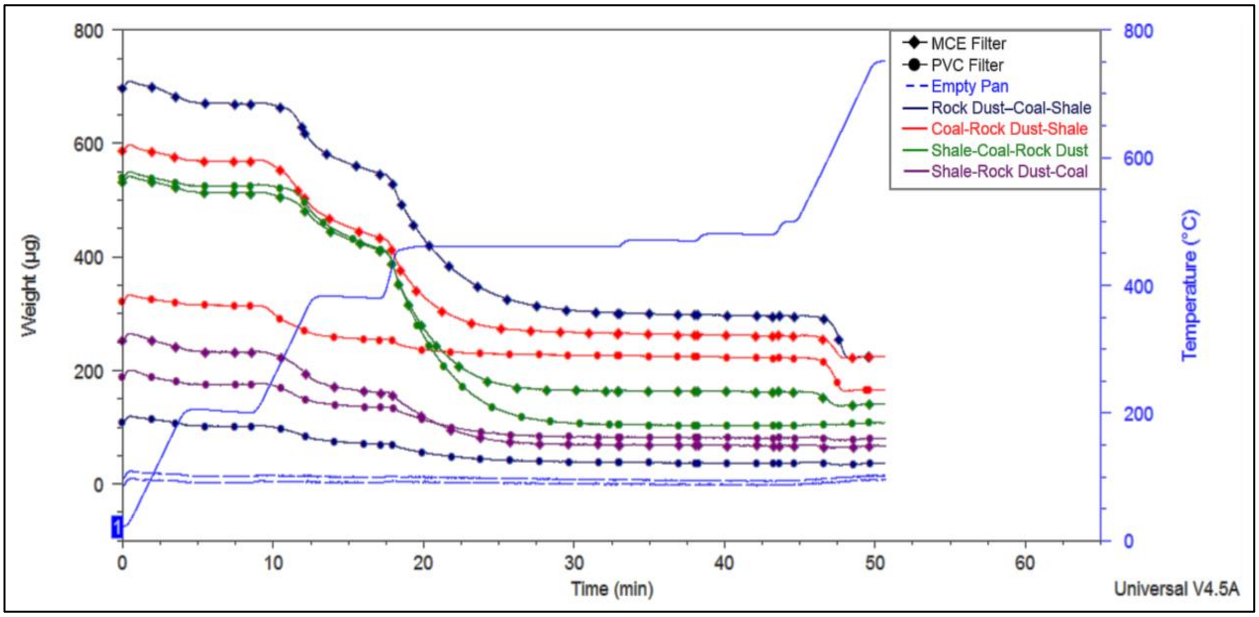

Figure 2.11. Example thermograms for lab-generated dust samples containing coal, rock dust, and shale materials.

Figure 2.12 shows TGA- versus gravimetrically derived coal, carbonate, and non-carbonate mineral mass fractions for all 43 samples as computed by Equations 2.10-2.12; and Figure 2.13 shows the results when carbonate and non-carbonate minerals fractions are combined to simply show the non-coal fraction. (A summary data table is also provided in Tables A.5 and A.6 of Appendix A.) The ability of the developed TGA method to estimate coal and non-coal mass fractions is fairly good, as indicated by the slopes and R^2 values of the trend lines shown in Figure 2.13. However, distinguishing the difference between carbonate and non-carbonate minerals is much more difficult – particularly for very small samples and/or those with very little observed CO_2 mass.

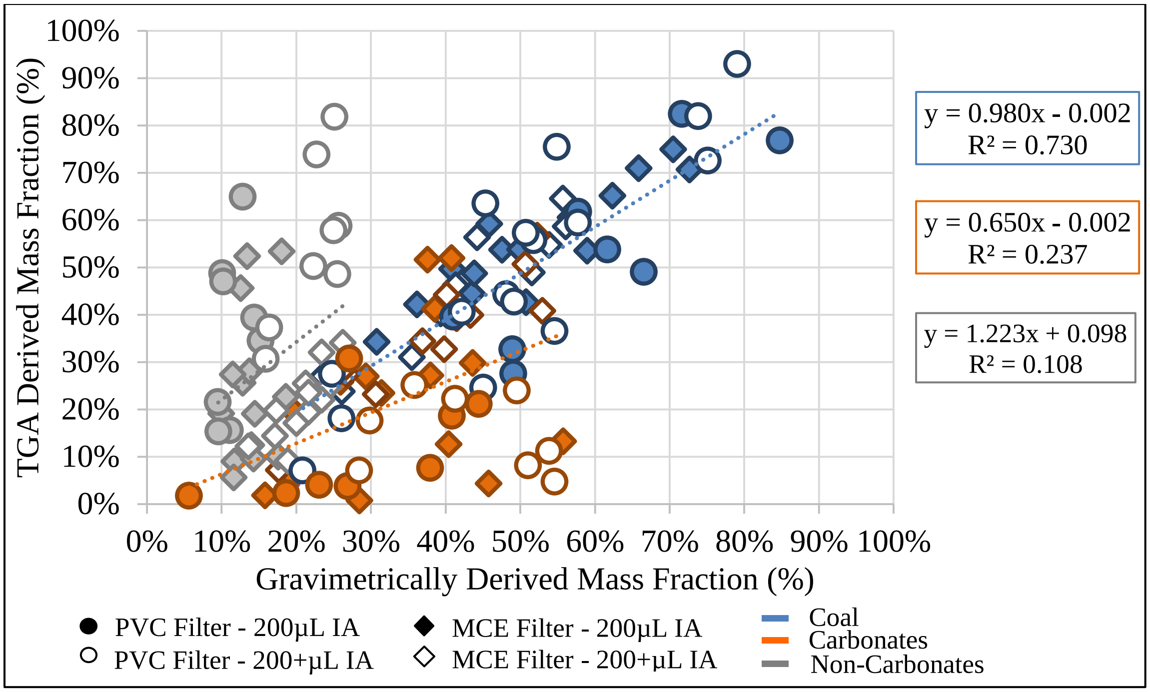

Figure 2.12. Comparison of gravimetric and TGA derived mass fractions for coal, carbonates, and non-carbonates particles. Trend lines include all data points (i.e., those prepared with 200uL and more than 200uL of IA).

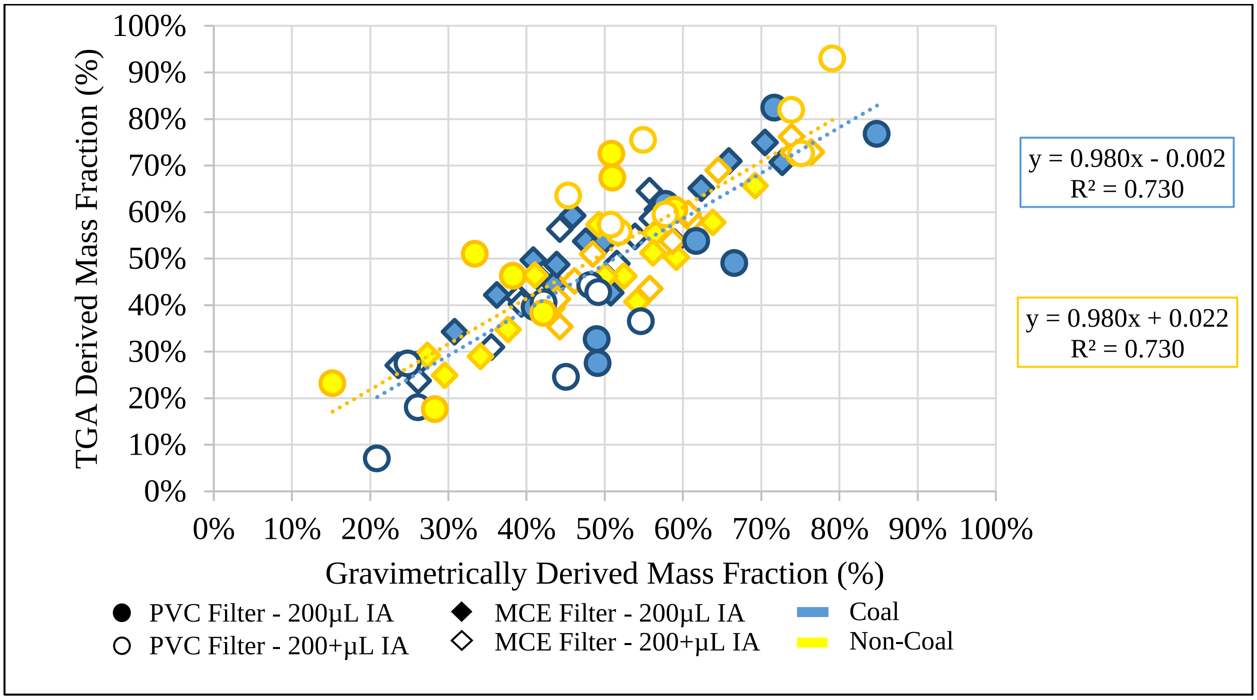

Figure 2.13. Comparison of gravimetric and TGA derived mass fractions for coal and non-coal particles. Trend lines include all data points (i.e., those prepared with 200uL and more than 200uL of IA).

Figure 2.14 shows the ratio of TGA- to gravimetrically-derived results for coal and non-coal mass fractions for all samples versus the dust mass recovered to the TGA pan from the sample filter. From this plot, it is evident that when only considering coal and non-coal mass fractions, relatively good accuracy can be achieved at even low sample masses (i.e., 50 μg or more). Generally, the TGA-derived mass fractions match the gravimetric values within about ± 25%. However, for determining the mass fractions of carbonates and non-carbonate minerals in addition to coal, there appear to be two key factors affecting the accuracy of the TGA results: observed CO_2 loss and total dust mass recovered to the TGA pan. To illustrate the relationship between these factors, Figure 2.15 shows the ratio of TGA- to gravimetrically-derived mass fractions for coal, carbonates and non-carbonate minerals for all of the lab-generated samples versus the product of observed CO_2 loss and total dust mass. When this product is about 3,500 μg^2 or more, the accuracy of the TGA results is generally within about ± 25% of the gravimetric values. So from a practical perspective, the carbonate and non-carbonate minerals mass fraction should only be reported for samples exhibiting a sufficiently large product between CO_2 loss and total dust mass. When the product is lower, it is still possible to calculate the carbonate mass fraction, but it is important to note that the computed value represents the minimum amount of carbonates present in the sample.

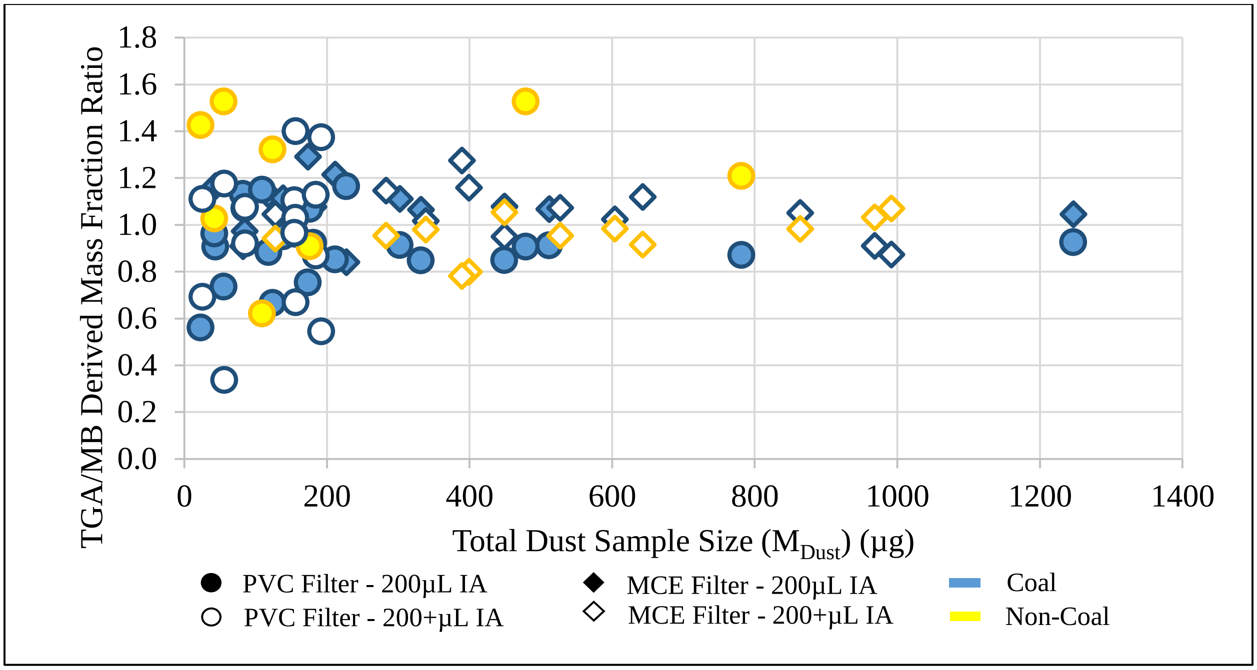

Figure 2.14. Ratio of TGA- to gravimetrically-derived dust mass fractions by the amount of dust recovered to TGA for lab generated samples containing coal, rock dust, and shale. All data points, including those prepared with 200uL and more than 200uL of IA, are included.

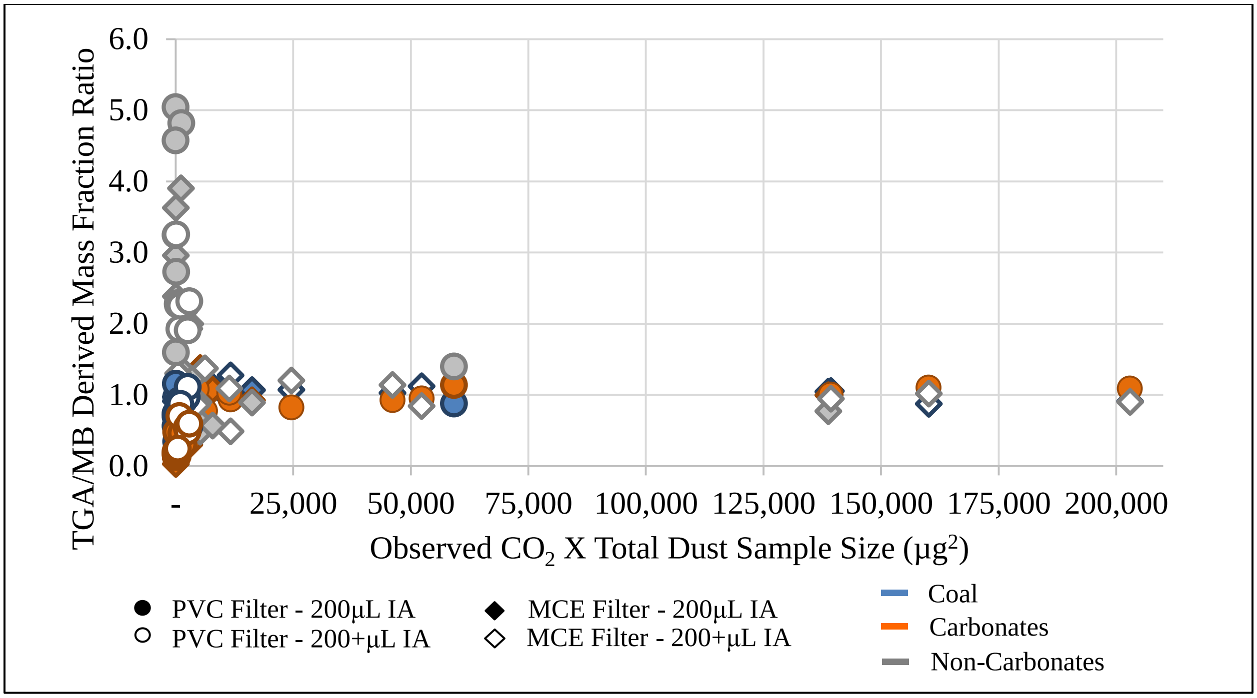

Figure 2.15. Ratio of TGA- to gravimetrically-derived dust mass fractions by the combined factors of observed CO_2 weight loss and the amount of dust recovered to TGA for lab generated samples containing coal, rock dust, and shale. All data points, including those prepared with 200uL and more than 200uL of IA, are included.

4. Conclusions

Considering the implications for occupational health, there is a real need to expand the present knowledge about respirable dust in underground coal mines. The dust-only TGA method described here allows for approximation of coal and non-coal dust mass fractions, even in the case where relatively little dust is recovered for analysis. From a health perspective, this method could be a powerful tool for examining the atmosphere in areas of a mine where dust particles differ from conventional categorical notions (i.e., particles are either coal or silica). Indeed, if silica is oftentimes associated with rock, identification of relatively high non-coal mass fractions may provide additional screening capabilities. If sufficient dust can be recovered, the method can also be used to distinguish between carbonate and non-carbonate minerals. With this information, it is possible to help determine the influence of carbonates (i.e. rock dust commonly used to coat the surfaces of the mine) has on the respirable fraction of dust present in the atmosphere. For the safety of the miners, this could help notify operators of rock dust being out of specification for particle size and pose additional risks for accumulation in the respiratory system.

As noted, dust recovery for analysis is key for the developed TGA method. While removing more dust from filters may present some challenges related to further premature carbonate loss (i.e., due to the sonication or other factors), additional efforts to recover dust removed from the filters appears promising. MCE filters appear to have some advantage over PVC with respect to dust recovery; although use of PVC filters, which are the standard for respirable quartz mass determination in coal mines, may allow the TGA method to be easily integrated with current analyses. Moreover, the method may well be adaptable for samples collected with CPDMs.

Future work should include use of this method to analyze samples collected in the field, and comparison to results from other analysis, such as SEM-EDX. This may help to define how various analytical methods may be used to complement one another. Additionally, such work will establish characteristics specific to regions of mining or localized in different areas of the mines for particular types of dust exposure. With implementation of the new dust rule, testing with CPDM filters should also be completed to understand how TGA may be applied to dust collected on these filters.

5. *Acknowledgements*

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Chapter 3. TGA of Preliminary Set of Field Samples and Recommendations for Future Work

1. Introduction

The purpose of the work presented in the preceding chapters was to develop and verify a method for characterization of respirable dust commonly observed in coal mines. Thermogravimetric analysis was implemented in a dust-only approach for approximation of coal and non-coal mass fractions, as well as coal, carbonate, and non-carbonate mass fractions with larger sample sizes. The comprehensive method was developed by means of bulk sample analysis with TGA to identify specific temperature ranges where dusts commonly observed in underground coal mines oxidize or thermally decompose. A dust-only method was applied in order to limit interference from the filter media and gain a more finite understanding of the chemical changes undergone by the dust constituents. During sample preparation, premature loss of CO_2 from carbonates was identified, and a correction was developed to adjust for this loss. Further correction for naturally occurring thermal drift in the TGA instrument was developed. Verification samples were analyzed and the results indicated that this method can provide powerful information about the dust constituents present in the working atmosphere. In this final chapter, results of the TGA on a preliminary set of field samples are presented.

2. Sample Collection

A field sampling campaign was undertaken to collect respirable dust samples underground coal mines throughout Appalachia. This impetus was to investigate dust characteristics in regions of Appalachia in relation to increases in the prevalence of occupational lung disease (CWHSP, 2014; CDC 2006 and 2007, dos Santao et al., 2005). Sampling was focused on three regions in Appalachia: northern Appalachia (NA), central Appalachia (CA), and south central Appalachia (SCA), which encompass mines in MSHA Districts 2 and 3, District 4, and District 12, respectively (CMSHD).

In the three regions, samples were collected in multiple locations for each mine. The locations were chosen to represent areas of high dust generation and accumulation, or common work areas for miners: the *Intake,* the *Return,* the *Feeder,* and near *Production Equipment* (e.g., continuous miners, roof bolters, and the longwall shear). All samples were collected in a manner analogous to compliance sampling practices by using the same equipment and handling practices for lab-generated samples (see Chapter 2). In the field, pumps were generally hung from roof bolts, which ensured that the inlet of the pump cyclone was placed at a height similar to that of one worn by a miner for compliance sampling. Samples were collected for a period of two to four hours, and a combination of PVC and MCE filters were collected for TGA; additional samples were gathered for complimentary analysis with SEM-EDX (see Sellaro, 2014, for method description). Notably, the sample collection times used here (vs. full shift) limits the accuracy of the carbonates correction presented in Chapter 2, due to smaller masses of dust loaded onto the filter. Thus, for this set of field samples, the carbonate mass fraction was not considered here.

This sampling process allowed for the two main test factors (i.e., mine region and sampling location) to be examined for their potential influence on the dust in the working atmosphere for miners. The field campaign gathered 148 area samples for TGA. Of these, a preliminary subset of 44 samples was analyzed to determine coal and non-coal mass fractions.

3. Results and Discussion

Figures 3.1-3 show the results of the TGA analysis on all 44 samples grouped by mine region, which are also presented numerically in Appendix B, Table B.1. Overall, the results reveal general trends for the mass fractions of coal and non-coal by the location and region in which they were gathered. NA mine samples largely had the highest levels of coal present in the sample along with the largest masses of dust deposited on the filters. The rise in total dust may be due to the higher rate of production by the longwall shear and a larger surface area of the seam exposed for production for the longwall generating a greater amount of coal dust in comparison to samples collected near a continuous miner. The CA region experienced the highest levels of non-coal in samples, which may be due to the practice of mining thinner coal seams with a larger portion of the surrounding rock strata to maintain competency of the mine. Participating mines from SCA were similar to those from CA with greater fractions of non-coal normally present in the samples in comparison to those from NA. However, from the subset analysis, more distinct characteristics were observed when comparing samples categorized by the area in the mine in which they were collected.

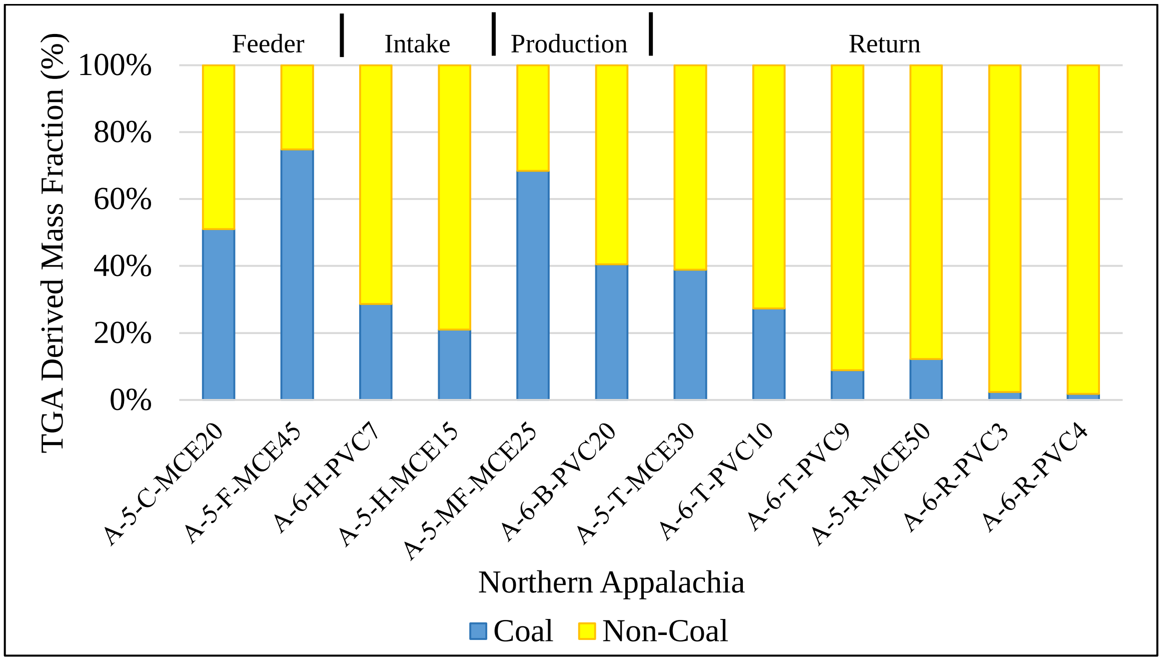

Figure 3.1. TGA derived mass fractions for coal and non-coal particles for field samples from northern Appalachia mines. Samples are named as Region-Mine-Sampling location-Filter number. Sampling locations were: feeder (F), intake (I), roof bolter (B), continuous miner (M), longwall headgate (H), longwall mid-face (MF), longwall tailgate (T), return (R).

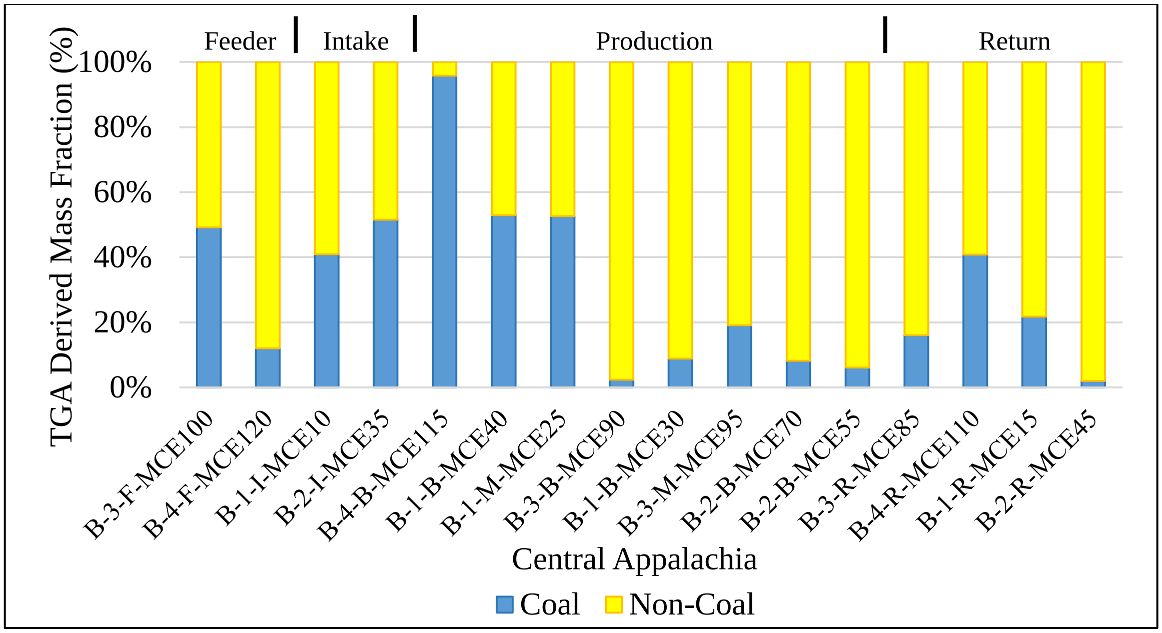

Figure 3.2. TGA derived mass fractions for coal and non-coal particles for field samples from central Appalachia mines. Samples are named as Region-Mine-Sampling location-Filter number. Sampling locations were: feeder (F), intake (I), roof bolter (B), continuous miner (M), longwall headgate (H), longwall mid-face (MF), longwall tailgate (T), return (R).

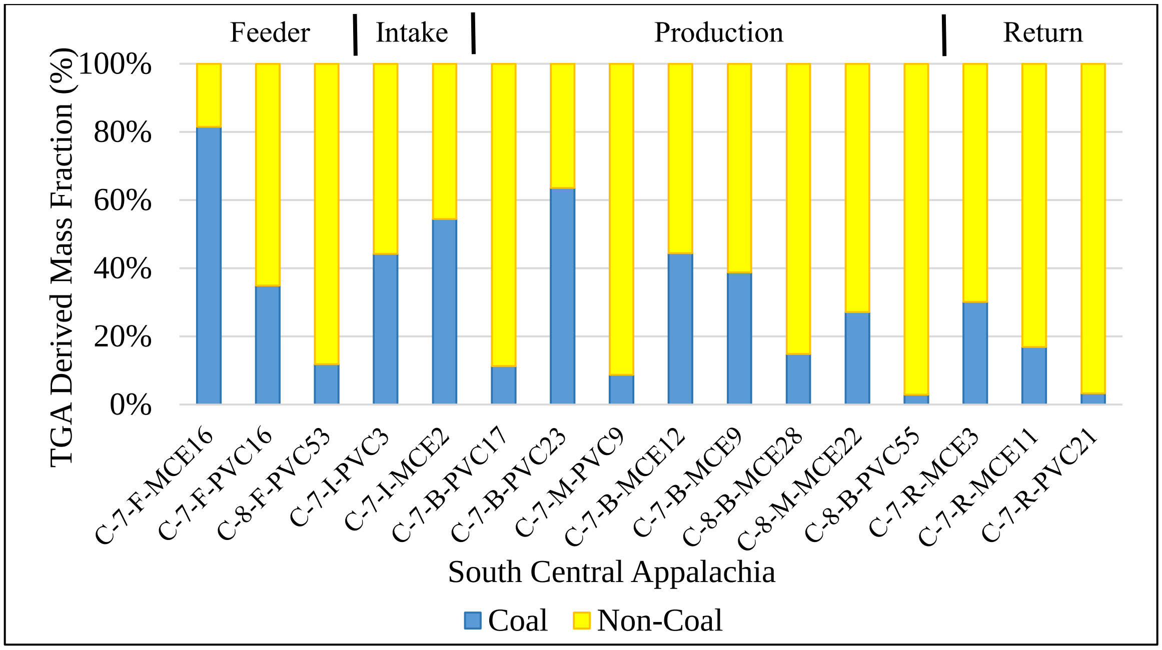

Figure 3.3. TGA derived mass fractions for coal and non-coal particles for field samples from south central Appalachia mines. Samples are named as Region-Mine-Sampling location-Filter number. Sampling locations were: feeder (F), intake (I), roof bolter (B), continuous miner (M), longwall headgate (H), longwall mid-face (MF), longwall tailgate (T), return (R).

Intake samples generally had the least amount of mass collected on the filters during the three hour sampling period and were a mixture of coal and non-coal particles. This suggests that the lack of moving equipment and production may limit the amount of airborne dust present in these areas of the mine. The lack of coal in the mass fraction of the sample may be due to rock dusting of the mine walls, commonly referred to as the roof, ribs, and floor, in order to mitigate the risk of a coal dust explosion. In contrast, *Feeder* samples were had more coal, suggesting that the movement of coal from the main production areas onto the conveyance systems in the mine create a localized area with higher levels of coal dust. *Production Equipment* samples had varied results for coal and non-coal mass fractions. This is most likely due to the nature of the different types of production equipment sampled (e.g., longwall shear, continuous miner, and roof bolter), and if the equipment was used for coal cutting versus rock cutting. The longwall shear and continuous miner are primarily designed for coal cutting as the main production equipment with some cutting of rock during the process. Roof bolters are intended as support equipment with the main purpose of drilling into rock for the application of roof control measures to increase the stability of the rock strata surrounding the coal seam. Thus, the non-coal mass fraction present in these samples could be influenced by the practice of excavating additional material from the strata surrounding the coal seams to increase the structural competency of the mine. However, for the purpose of this study, all equipment used in the production locations of the mines operated in such close proximity and with the potential mixture of dust from multiple pieces of equipment due to ventilation practices, the samples were combined into one category. *Return* samples contained the lowest fractions of coal from the samples. Common practice employs the use of trickle dusters to coat the *Return* in rock dust (i.e., carbonates) in order to mitigate the accumulation of coal dust which can influence the mass fraction ratios of coal and non-coal present in these areas of the mine leading to some *Return* samples containing very high non-coal and carbonate mass fractions.

For a more in depth review of the results of the sampling campaign, a statistical analysis was completed to determine any main effects correlated to the primary test factors (i.e., region and sampling location) in the subset. No significant effects were found when comparing the regions in which samples were gathered for coal and non-coal mass fractions for the subset of samples (see Table B.2 in Appendix B for analytical results). Conversely, sampling location (i.e. *Intake*, *Feeder*, *Production Equipment*, and *Return*) appeared to have a significant effect on the coal and non-coal mass fractions observed in the samples (F=2.89, $p<0.05$) (see Table B.3 for analytical results). Further analysis by means of two sample t-tests with unequal variance was conducted to compare the coal mass fraction by location. From the comparison of the sample locations, the *Return* had statistically significant different coal mass fractions from those of the *Intake* (t=1.81, $p<0.05$), *Production Equipment* (t=1.70, $p<0.05$), and the *Feeder* (t=1.85, $p<0.05$) (see Table B.4 in Appendix B for complete t-test results). These results suggest that the *Return* has significantly lower fractions of coal in comparison to the fractions observed for all other sampling locations. This trend may be influenced by the total mass and characteristics of the dust gathered in these locations. As *Return* samples are gathered in the exhausting air of the mine, the largest concentration of dust present in the atmosphere is found in this location. The dust present in these areas is a combination of the dust generated in the mine from rock dust, coal, and surrounding rock strata. Some mines participating in the study also employed trickle dusters to coat the return in rock dust to mitigate the propagation of coal dust, which may increase the amount of non-coal particles in the atmosphere and thus increase the non-coal mass fraction present in *Return* samples.

4. Conclusions

From the field sampling campaign, preliminary analysis has revealed valuable information about dust characteristics in underground coal mines throughout Appalachia. Specifically, the sampling location in the mine appears to have a significant impact on the type of dust, coal or non-coal, present in the samples. The field sampling campaign has also shown how the TGA method may be incorporated into compliance sampling practices and help increase knowledge about the health risks associated with exposure to respirable dust. Even with current progress made for respirable dust analysis with TGA, there may be others factors influencing the mass fractions of coal and non-coal present in the samples and more work is suggested with the results from this research to further understand mass fraction analysis of respirable dust in mines.

5. References

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Chapter 4. Conclusions and Future Work

The purpose of this project was to develop and implement a method with thermogravimetric analysis for further investigation and characterization of respirable coal mine dust. Development of the method involved bulk sample analysis with TGA of materials thought to be commonly found in underground coal mines and determination of temperature ranges where the materials may oxidize or thermally decompose. Preliminary testing and verification of the method was completed with samples generated in the lab in a manner analogous to those collected for compliance purposes. From the method development and verification process, a dust-only approach was determined and a correction for premature decomposition of carbonates was established. A field sampling campaign was established to investigate and identify dust characteristics in distinct regions in Appalachia. Samples were collected in various locations noted for high concentrations of respirable dust along with common work areas for miners. Results from the analysis of a subset of the field samples reveal that while there is no significant difference between mining regions, the location in the mine where the sample was collected is significant and trends may be identified for sampling locations for the concentration of coal and non-coal present in the atmosphere. The collection and analysis of the field samples can provide valuable information and further insight about the characteristics of respirable dust in underground coal mines. Indeed, considerable progress has been accomplished for respirable dust characterization with method development and implementation with field samples, future work is recommended from current results.

For the continuation of this work, there several topics that could be further investigated. Possible adjustments could be made to correction for carbonates based on TGA sample size and observed CO_2 weight loss. Analysis of all field samples collected in varying locations in underground mines and by miners should be completed to increase the current understanding of mine location and region dust characteristics. Comparison of mine samples analyzed with TGA along with paired samples analyzed with SEM-EDX should be completed to verify similarities between the methods and trends in the data. Additional exploration of the effects of sonication and TGA with CPDM samples is encouraged with the implementation of this filter for future compliance sampling. After full analysis of the samples gathered in mines and by miner volunteers, mine operators and miners should be informed of high exposure risks found by the location in the mine and by occupation as well as additional work to limit the exposures. This valuable information may give further insight about the characteristics of respirable dust in underground coal mines and the associated health risks.

Appendix A. Chapter 2 Supplemental Data

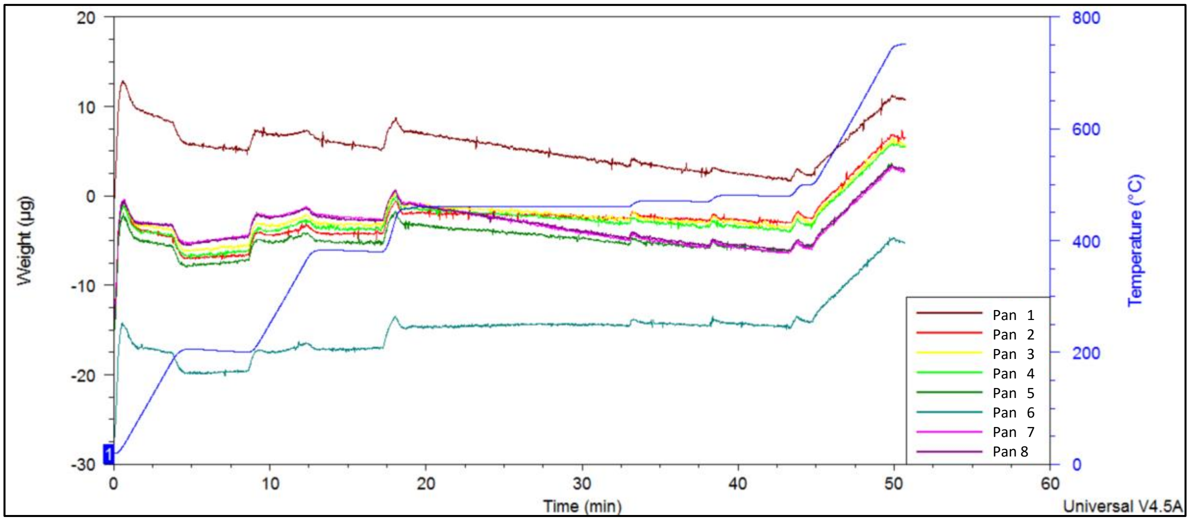

Figure A.1. Example Thermogram for Empty Pan Weight Change in TGA Method.

Table A.1. TGA Empty Pan Weights at Specific Temperatures for Calibration

Time (min)	**0 min**	**3.55 min**	**8.58 min**	**9.53 min**	**10.95 min**	**12.20 min**	**17.19 min**	**32.95 min**	**43.29 min**	**52 min**
Temperature (°C)	**Amb.**	**179°C**	**200°C**	**230°C**	**300°C**	**360°C**	**380°C**	**460°C**	**480°C**	**750°C**
-	µg	µg	µg	µg	µg	µg	µg	µg	µg	µg
Pan 1	0.182 ±1.843	8.372 ±2.070	5.039 ±2.251	7.118 ±2.363	6.758 ±2.646	7.183 ±2.780	4.960 ±3.075	1.899 ±3.892	0.507 ±2.998	9.523 ±3.359
Pan 2	-9.551 ±5.142	-2.693 ±2.062	-5.551 ±2.880	-3.498 ±3.156	-4.010 ±4.416	-3.522 ±5.020	-4.166 ±5.468	-2.752 ±6.545	-3.312 ±6.345	6.526 ±6.468
Pan 3	-15.103 ±4.058	-7.004 ±6.770	-9.078 ±8.322	-6.867 ±8.567	-7.005 ±9.426	-6.376 ±9.903	-7.261 ±9.649	-6.459 ±7.370	-7.040 ±6.389	2.676 ±5.937
Pan 4	-15.375 ±2.281	-6.154 ±3.925	-7.966 ±4.672	-5.660 ±4.786	-5.559 ±5.222	-4.877 ±5.469	-5.728 ±5.432	-5.206 ±3.562	-6.156 ±3.278	3.625 ±2.996
Pan 5	-15.113 ±2.145	-6.159 ±3.464	-7.569 ±4.396	-5.432 ±4.677	-5.365 ±4.844	-4.560 ±5.121	-5.790 ±4.882	-6.190 ±3.201	-7.083 ±2.571	2.478 ±2.515
Pan 6	-15.813 ±2.200*	-9.669 ±5.627	-11.652 ±5.928	-9.408 ±5.979	-9.437 ±6.120	-8.733 ±6.179	-9.549 ±6.050	-8.724 ±5.301	-9.285 ±5.205	0.375 ±5.348
Pan 7	-16.100 ±3.067	-7.616 ±5.107	-9.756 ±6.035	-7.478 ±6.156	-7.552 ±6.581	-6.849 ±6.822	-7.610 ±6.810	-5.866 ±5.648	-6.189 ±5.235	3.523 ±5.222
Pan 8	-14.978 ±2.964	-5.900 ±3.992	-7.527 ±4.517	-5.161 ±4.935	-5.038 ±4.935	-4.426 ±5.112	-5.451 ±4.904	-5.862 ±2.862	-6.849 ±2.041	2.676 ±1.850

*Initial pan weight for one run had residue from previous runs, creating an abnormal amount of weight and was removed from the normalized weight for Pan 6 at ambient temperature.

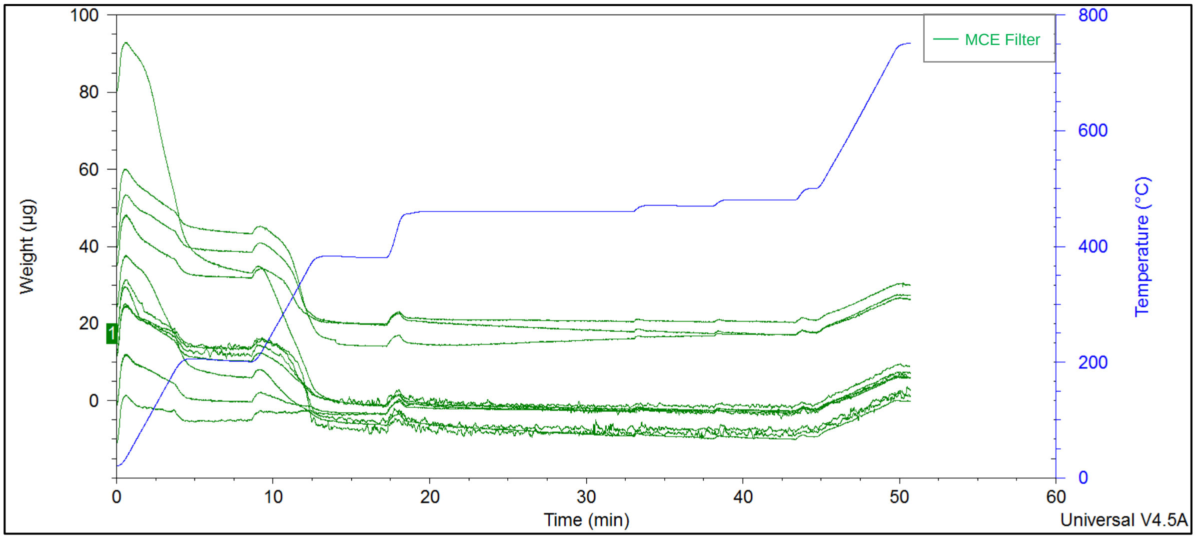

Figure A.2. Example thermograms for residue from sonication of blank MCE filters run in ELF Pumps for 55 or 110 minutes in TGA Method.

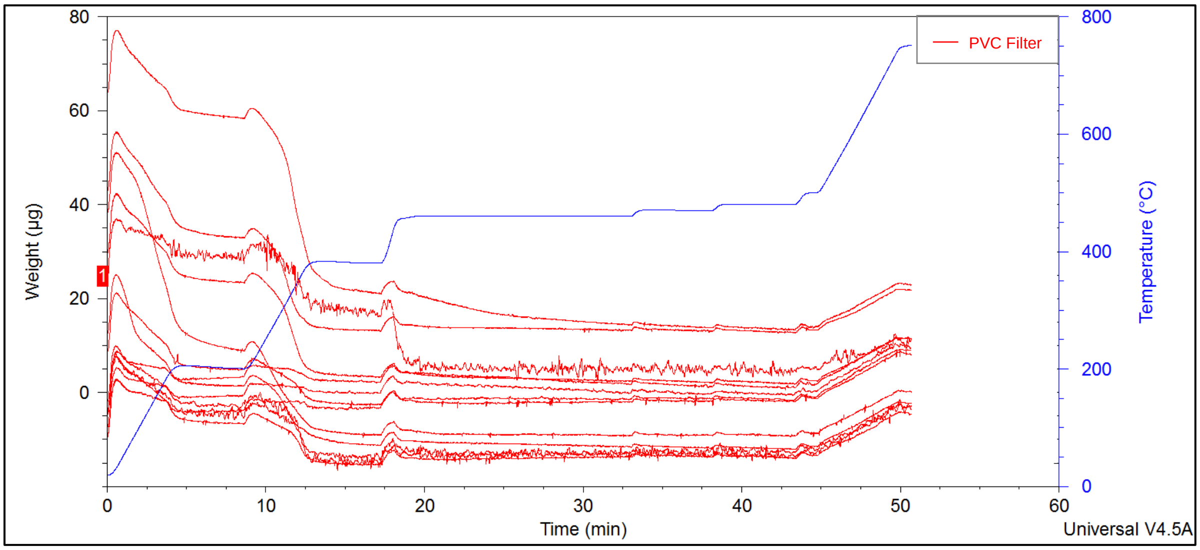

Figure A.3. Example thermograms for residue from sonication of blank PVC filters run in ELF Pumps for 55 or 110 minutes in TGA Method.

Table A.2. Blank MCE and PVC filter weights normalized with the maximum value of the last three readings subtracted from the weights

	0 min	**3.55 min**	**8.58 min**	**9.53 min**	**10.95 min**	**12.20 min**	**17.19 min**	**32.95 min**	**43.29 min**	**52 min**
Filter	**at Amb.**	**179 °C**	**200 °C**	**230°C**	**300°C**	**360°C**	**380°C**	**460°C**	**480°C**	**750°C**
Type	**µg**	**µg**	**µg**	**µg**	**µg**	**µg**	**µg**	**µg**	**µg**	**µg**
MCE-1	30.69	26.68	21.37	21.47	15.77	2.47	0.37	0.00	0.00	0.00
MCE-2	30.99	31.85	28.50	27.89	22.09	4.16	0.00	0.00	0.00	0.00
MCE-3	28.36	22.70	20.56	20.36	15.88	7.53	5.75	0.00	0.00	0.00
MCE-4	26.96	18.76	15.74	15.19	11.50	6.57	2.69	0.00	0.00	0.00
MCE-10	30.04	26.26	22.59	22.26	19.46	5.61	0.00	0.00	0.00	0.00
MCE-11	24.28	24.28	20.72	20.73	16.45	7.09	0.49	0.00	0.00	0.00
MCE-12	31.87	24.83	22.11	21.39	16.96	7.63	4.02	0.00	0.00	0.00
MCE-13	91.59	57.51	36.27	33.81	19.35	6.18	0.00	0.00	0.00	0.00
MCE-14	8.09	7.95	4.41	3.78	1.54	0.00	0.00	0.00	0.00	0.00
MCE-15	45.33	30.77	20.23	18.72	12.41	7.71	4.53	0.00	0.00	0.00
MCE-16	47.87	27.94	17.56	16.39	10.50	2.81	0.00	0.00	0.00	0.00
MCE-18	21.42	19.04	16.78	16.13	13.48	8.25	4.40	0.00	0.00	0.00
PVC-1	38.04	32.99	29.47	29.11	23.70	12.09	8.33	0.00	0.00	0.00
PVC-2	35.15	29.54	25.19	24.69	19.54	6.35	3.30	0.00	0.00	0.00
PVC-3	63.64	55.29	50.41	49.15	41.66	22.39	9.58	0.00	0.00	0.00
PVC-4	33.60	19.85	16.00	15.39	10.72	3.47	0.07	0.00	0.00	0.00
PVC-10	28.78	29.80	28.22	28.78	27.14	20.49	14.52	0.00	0.00	0.00
PVC-11	19.81	15.17	13.35	12.25	9.43	2.78	0.00	0.00	0.00	0.00
PVC-12	17.35	12.29	8.45	8.54	6.22	0.37	0.00	0.00	0.00	0.00
PVC-13	19.67	14.68	11.84	11.46	9.58	5.20	2.16	0.00	0.00	0.00
PVC-14	17.00	12.04	8.45	8.02	5.61	0.00	0.00	0.00	0.00	0.00
PVC-15	58.38	34.45	20.80	18.97	9.53	2.84	0.00	0.00	0.00	0.00
PVC-16	17.35	16.47	15.62	15.56	14.14	6.89	1.22	0.00	0.00	0.00
PVC-17	18.34	16.99	15.33	15.16	13.91	4.75	0.00	0.00	0.00	0.00
PVC-18	57.18	38.96	29.41	28.09	22.44	10.44	1.46	0.00	0.00	0.00
Avg. MCE	**34.79 ±20.62**	**26.55 ±11.65**	**20.57 ±7.54**	**19.84 ±7.25**	**14.62 ±5.37**	**5.50 ±2.59**	**1.85 ±2.25**	-	-	-
Avg. PVC	**32.63 ±17.14**	**25.27 ±12.93**	**20.97 ±11.62**	**20.40 ±11. 43**	**16.43 ±10.24**	**7.54 ±7.08**	**3.13 ±4.69**	-	-	-

**As the average weight change in the 460-750ºC temperature region is around 2% of the filter residue, this amounts to micrograms of weight change and is not considered as an interference for determination of carbonate and non-carbonate minerals.*

Table A.3. Blank MCE and PVC filter normalized weight change percentages with data from Table A.2.*

Filter Type	**Amb. -360°C**	**360°C - 480°C**	**480°C - 750°C**	**750°C**
	%	**%**	**%**	**%**
MCE-1	91.96	8.04	0.00	0.00
MCE-2	86.57	13.43	0.00	0.00
MCE-3	73.44	26.56	0.00	0.00
MCE-4	75.64	24.36	0.00	0.00
MCE-10	81.33	18.67	0.00	0.00
MCE-11	70.78	29.22	0.00	0.00
MCE-12	76.07	23.93	0.00	0.00
MCE-13	93.25	6.75	0.00	0.00
MCE-14	100.00	0.00	0.00	0.00
MCE-15	83.00	17.00	0.00	0.00
MCE-16	94.13	5.87	0.00	0.00
MCE-18	61.47	38.53	0.00	0.00
PVC-1	68.22	31.78	0.00	0.00
PVC-2	81.93	18.07	0.00	0.00
PVC-3	64.82	35.18	0.00	0.00
PVC-4	89.66	10.34	0.00	0.00
PVC-10	28.81	71.19	0.00	0.00
PVC-11	85.97	14.03	0.00	0.00
PVC-12	97.87	2.13	0.00	0.00
PVC-13	73.59	26.41	0.00	0.00
PVC-14	100.00	0.00	0.00	0.00
PVC-15	95.13	4.87	0.00	0.00
PVC-16	60.26	39.74	0.00	0.00
PVC-17	74.10	25.90	0.00	0.00
PVC-18	81.75	18.25	0.00	0.00
Avg. MCE	**82.30 ±11.34**	**17.70 ±11.34**	**-**	**-**
Avg. PVC	**77.09 ±19.21**	**22.91 ±19.21**	**-**	**-**

**As the average weight change in the 460-750ºC temperature region is around 2% of the filter residue, this amounts to micrograms of weight change and is not considered as an interference for determination of carbonate and non-carbonate minerals so it is not included in this analysis.*

Table A.4. Blank MCE and PVC filter residues with upper and lower limits for 95% confidence intertvals

Filter Recovery						
Filter Type	0-360℃			360-480℃		
	Average	95% C.I.		Average	95% C.I.	
		Lower Limit	Upper Limit		Lower Limit	Upper Limit
MCE	85.5	78.7	92.6	14.5	7.4	21.5
PVC	77.1	66.5	87.72	22.9	12.3	33.5

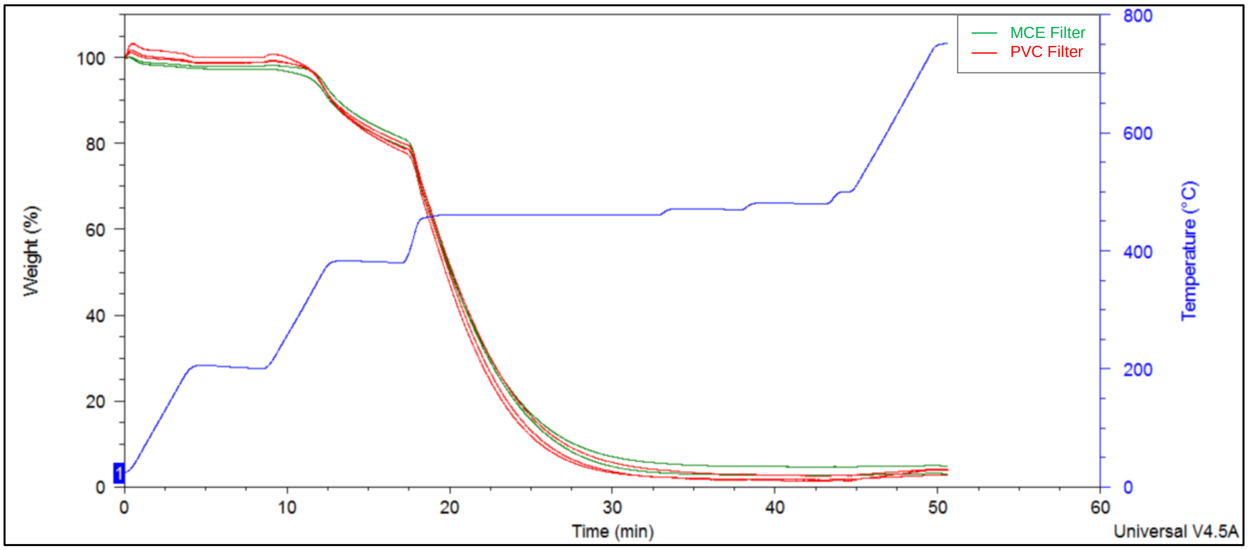

Figure A.4. Weight percent for coal only dust samples for PVC and MCE filters.

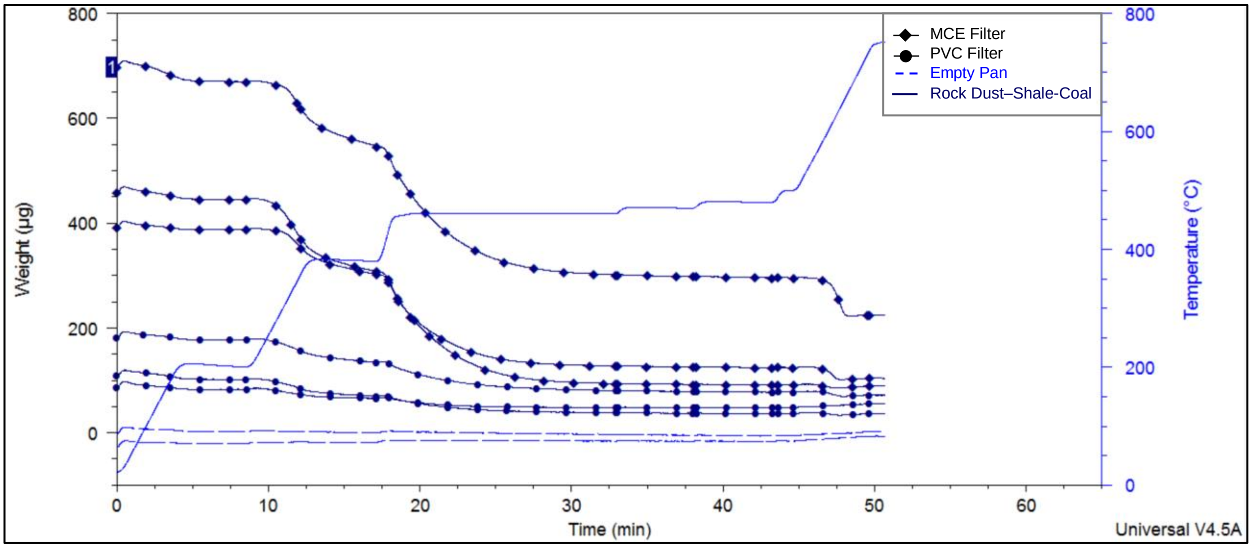

Figure A.5. Thermograms for three component samples collected in the order of rock dust – shale – coal.

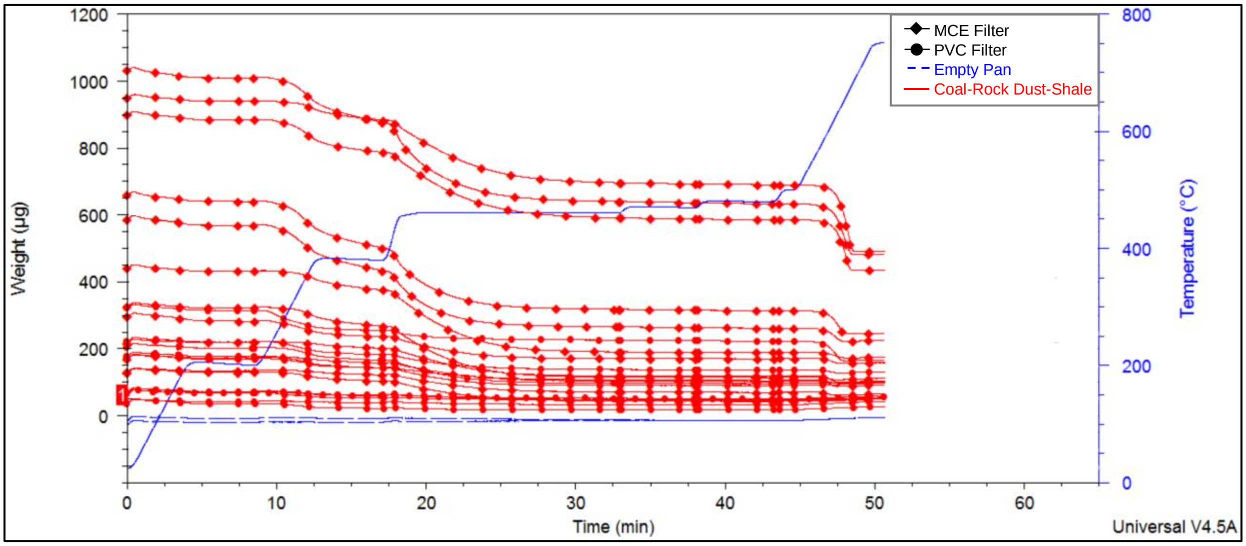

Figure A.6. Thermograms for three component samples collected in the order of coal – rock dust – shale.

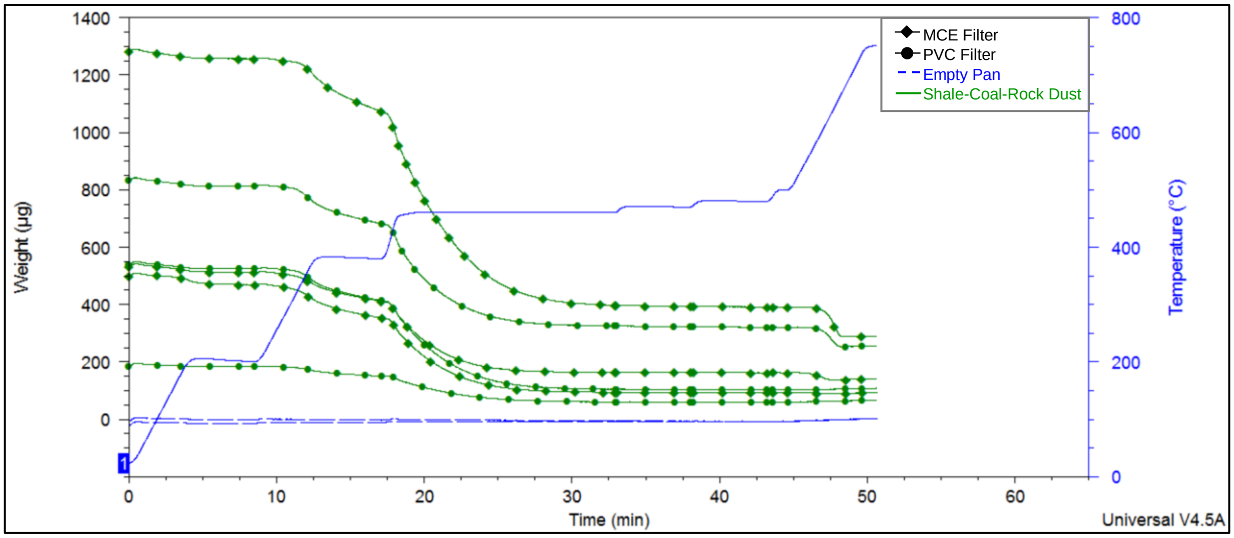

Figure A.7. Thermograms for three component samples collected in the order of shale – coal – rock dust.

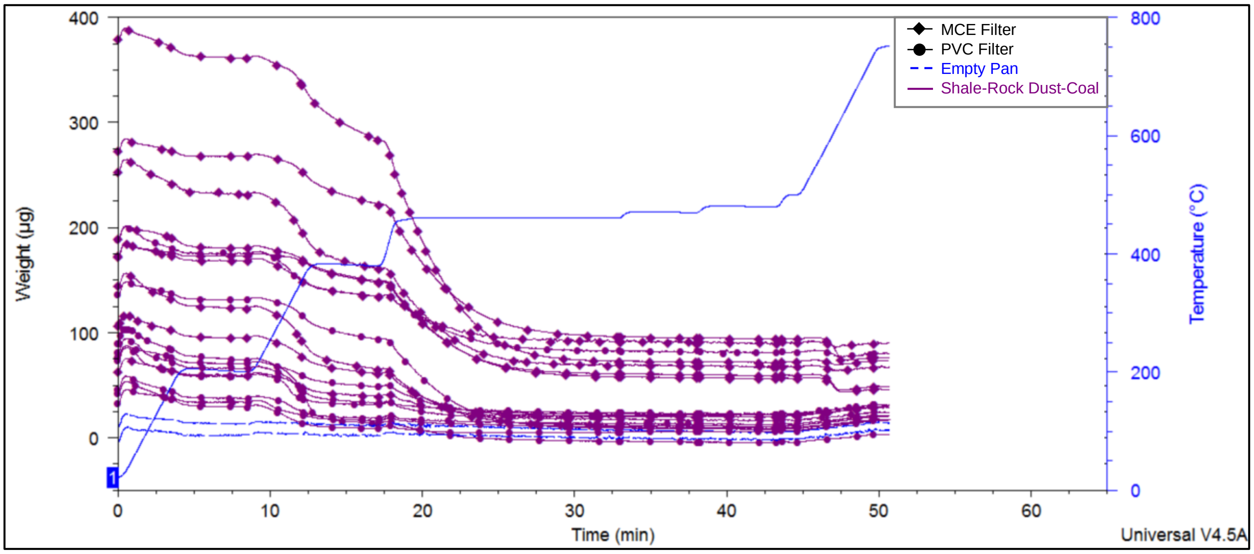

Figure A.8. Thermograms for three component samples collected in the order of shale – rock dust – coal.

Table A.5. Results from TGA analysis of three component verification samples compared to original gravimetrically derived mass fractions

Sample Name	Gravimetrically Derived					TGA Derived							TGA/Gravimetrically Derived							
	Mass Fraction				Dust Recovery	Mass Fraction				TGA Sample Size	Observed CO_2 Loss	Observed CO_2 Loss X TGA Sample Size	Mass Fraction Ratio				Mass Fraction Percent Error			
	Coal	Carbonate	Non-Carbonate	Non-Coal		Coal	Carbonate	Non-Carbonate	Non-Coal				Coal	Carbonate	Non-Carbonate	Non-Coal	Coal	Carbonate	Non-Carbonate	Non-Coal
	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(μg)	(μg)	(μg^2)	-	-	-	-	(%)	(%)	(%)	(%)
121515CASPVC5	49.13	38.00	12.87	50.87	6.97	27.51	7.60	64.89	72.49	23	1	18	0.56	0.20	5.04	1.42	-44.00	-80.00	404.04	42.50
CAS021116PVC1	26.12	51.10	22.78	73.88	6.21	18.05	8.12	73.82	81.95	26	1	24	0.69	0.16	3.24	1.11	-30.88	-84.10	224.12	10.92
121515CASMCE11	58.95	28.46	12.59	41.05	17.15	53.54	0.80	45.66	46.46	82	0	24	0.91	0.03	3.63	1.13	-9.18	-97.19	262.74	13.18
121515CASMCE8	36.18	45.75	18.07	63.82	15.34	42.19	4.38	53.43	57.81	44	1	38	1.17	0.10	2.96	0.91	16.62	-90.43	195.72	-9.42
121515CASPVC10	66.59	23.13	10.28	33.41	5.16	49.00	4.00	47.00	51.00	55	1	55	0.74	0.17	4.57	1.53	-26.42	-82.69	357.16	52.66
121515CASMCE10	72.68	15.84	11.48	27.32	14.95	70.75	1.88	27.37	29.25	84	1	60	0.97	0.12	2.38	1.07	-2.65	-88.13	138.33	7.04
121515CASPVC12	71.70	18.70	9.60	28.30	7.01	82.42	2.28	15.30	17.58	109	1	122	1.15	0.12	1.59	0.62	14.95	-87.80	59.37	-37.89
CAS021116PVC3	20.90	53.93	25.16	79.10	7.71	7.03	11.15	81.82	92.97	56	3	158	0.34	0.21	3.25	1.18	-66.35	-79.33	225.15	17.54
CAS110615PVC1	41.07	44.50	14.43	58.93	4.02	39.54	21.13	39.33	60.46	42	4	172	0.96	0.47	2.73	1.03	-3.74	-52.51	172.55	2.61
CAS021116PVC4	54.63	19.63	25.74	45.37	15.46	36.52	4.72	58.76	63.48	156	3	518	0.67	0.24	2.28	1.40	-33.15	-75.98	128.33	39.91
CAS110515PVC2	57.82	26.91	15.27	42.18	10.81	61.73	3.75	34.52	38.27	176	3	524	1.07	0.14	2.26	0.91	6.76	-86.05	126.06	-9.27
CAS022216MCE5	56.09	17.67	26.24	43.91	19.68	58.66	7.22	34.12	41.34	128	4	529	1.05	0.41	1.30	0.94	4.59	-59.15	30.02	-5.86
CAS092315PVC1	48.18	35.88	15.94	51.82	12.59	44.29	25.08	30.63	55.71	85	10	824	0.92	0.70	1.92	1.07	-8.07	-30.11	92.18	7.50
CAS021116PVC5	49.20	28.46	22.33	50.80	18.01	42.73	7.04	50.24	57.27	185	6	1,080	0.87	0.25	2.25	1.13	-13.16	-75.28	124.95	12.75
121515CASMCE9	30.80	55.77	13.43	69.20	19.98	34.29	13.29	52.42	65.71	138	8	1,143	1.11	0.24	3.90	0.95	11.35	-76.17	290.23	-5.05
121515CASPVC8	49.00	40.88	10.12	51.00	8.43	32.64	18.62	48.74	67.36	124	10	1,289	0.67	0.46	4.82	1.32	-33.39	-54.44	381.51	32.08
121515CASMCE7	45.87	40.40	13.73	54.13	30.66	59.25	12.65	28.11	40.75	173	10	1,712	1.29	0.31	2.05	0.75	29.15	-68.70	104.78	-24.71
CAS110615MCE2	47.57	37.99	14.45	52.43	9.72	53.73	27.19	19.09	46.27	118	14	1,716	1.13	0.72	1.32	0.88	12.95	-28.43	32.11	-11.75
CAS110515PVC1	84.81	5.66	9.53	15.19	27.89	76.81	1.70	21.50	23.19	479	4	1,751	0.91	0.30	2.26	1.53	-9.43	-70.04	125.50	52.66
CAS092315PVC3	42.22	41.33	16.45	57.78	16.93	40.56	22.18	37.26	59.44	156	16	2,429	0.96	0.54	2.27	1.03	-3.93	-46.33	126.50	2.87
CAS021116PVC2	24.84	49.59	25.57	75.16	18.07	27.44	23.97	48.59	72.56	155	17	2,582	1.10	0.48	1.90	0.97	10.48	-51.66	90.01	-3.46
121515CASMCE12	70.49	19.57	9.94	29.51	19.78	75.00	5.82	19.18	25.00	332	9	2,886	1.06	0.30	1.93	0.85	6.41	-70.27	92.86	-15.30
CAS021116PVC6	45.07	29.89	25.04	54.93	16.74	24.54	17.63	57.83	75.46	192	15	2,939	0.54	0.59	2.31	1.37	-45.55	-41.03	131.00	37.37
CAS110615MCE3	43.53	43.62	12.85	56.47	11.34	44.52	29.86	25.62	55.48	151	20	3,070	1.02	0.68	1.99	0.98	2.28	-31.56	99.45	-1.75

121515CASMCE4	49.96	31.42	18.61	50.04	15.88	53.84	23.50	22.66	46.16	181	19	3,470	1.08	0.75	1.22	0.92	7.76	-25.22	21.76	-7.74
121515CASMCE6	40.87	40.81	18.32	59.13	16.64	49.68	51.99	(1.67)	50.32	211	20	3,562	1.22	1.27	-0.09	0.85	21.55	27.38	-109.10	-14.89
CAS110515MCE3	65.87	19.83	14.30	34.13	33.54	71.01	19.34	9.65	28.99	449	10	4,051	1.08	0.98	0.67	0.85	7.80	-2.48	-32.52	-15.06
CAS022216MCE6	53.85	26.11	20.04	46.15	40.63	54.76	28.13	17.11	45.24	338	13	4,096	1.02	1.08	0.85	0.98	1.68	7.75	-14.60	-1.96
CAS092315MCE2	55.73	30.67	13.60	44.27	49.90	64.58	23.23	12.19	35.42	399	12	4,503	1.16	0.76	0.90	0.80	15.89	-24.27	-10.38	-20.00
CAS110615MCE1	50.77	37.61	11.62	49.23	15.02	42.69	51.69	5.62	57.31	227	23	4,509	0.84	1.37	0.48	1.16	-15.91	37.46	-51.69	16.41
CAS021116MCE3	23.61	52.97	23.42	76.39	41.79	27.08	40.83	32.09	72.92	283	22	5,584	1.15	0.77	1.37	0.95	14.71	-22.92	37.01	-4.55
121515CASMCE5	43.84	38.56	17.60	56.16	34.14	48.74	41.25	10.01	51.26	302	26	7,074	1.11	1.07	0.57	0.91	11.17	6.98	-43.12	-8.72
CAS022216MCE4	51.55	26.80	21.65	48.45	49.58	48.98	27.49	23.53	51.02	449	25	10,653	0.95	1.03	1.09	1.05	-4.98	2.59	8.66	5.30
CAS092315MCE3	44.25	36.90	18.86	55.75	55.44	56.39	34.43	9.18	43.61	389	30	10,789	1.27	0.93	0.49	0.78	27.45	-6.68	-51.32	-21.78
CAS110515MCE2	56.72	29.30	13.98	43.28	30.48	60.55	26.98	12.47	39.45	512	32	15,286	1.07	0.92	0.89	0.91	6.76	-7.94	-10.77	-8.86
CAS103015MCE1	38.92	39.83	21.25	61.08	47.97	41.73	32.74	25.53	58.27	527	47	23,166	1.07	0.82	1.20	0.95	7.22	-17.79	20.13	-4.60
CAS103015MCE2	39.34	43.32	17.34	60.66	45.51	40.28	39.98	19.74	59.72	604	76	43,650	1.02	0.92	1.14	0.98	2.41	-7.71	13.80	-1.56
CAS092315MCE1	41.34	41.51	17.15	58.66	64.12	46.27	39.31	14.43	53.73	643	81	49,664	1.12	0.95	0.84	0.92	11.90	-5.30	-15.87	-8.39
CAS110515PVC3	61.71	27.12	11.17	38.29	32.40	53.74	30.70	15.55	46.26	781	76	56,772	0.87	1.13	1.39	1.21	-12.91	13.21	39.25	20.81
CAS021116MCE1	25.88	50.69	23.42	74.12	42.78	27.22	50.69	22.09	72.78	864	161	133,541	1.05	1.00	0.94	0.98	5.16	0.00	-5.70	-1.80
CAS110515MCE1	62.35	25.95	11.70	37.65	47.69	65.19	25.82	8.99	34.81	1,247	111	135,018	1.05	1.00	0.77	0.92	4.55	-0.48	-23.16	-7.53
CAS103015MCE3	35.50	40.17	24.33	64.50	60.75	31.02	44.20	24.78	68.98	992	161	154,352	0.87	1.10	1.02	1.07	-12.61	10.04	1.83	6.94

Table A.6. Results from TGA analysis of three component verification samples categorized into size classes and compared to original gravimetrically derived mass fractions

Observed CO_2 Loss X TGA Sample Size Class		**Gravimetrically Derived**					**TGA Derived**							**TGA/Gravimetrically Derived**							
		Mass Fraction				**Dust Recovery**	**Mass Fraction**				**TGA Sample Size**	**Observed CO_2 Loss**	**Observed CO_2 Loss X TGA Sample Size**	**Mass Fraction Ratio**				**Mass Fraction Percent Error**			
		Coal	**Carbonate**	**Non-Carbonate**	**Non-Coal**		**Coal**	**Carbonate**	**Non-Carbonate**	**Non-Coal**				**Coal**	**Carbonate**	**Non-Carbonate**	**Non-Coal**	**Coal**	**Carbonate**	**Non-Carbonate**	**Non-Coal**
(μg^2)		**(%)**	**(%)**	**(%)**	**(%)**	**(%)**	**(%)**	**(%)**	**(%)**	**(%)**	**(μg)**	**(μg)**	**(μg^2)**	**-**	**-**	**-**	**-**	**(%)**	**(%)**	**(%)**	**(%)**
0 – 100 (n=7)	**Avg.**	**54.48**	**31.57**	**13.95**	**45.52**	**10.40**	**49.07**	**4.15**	**46.78**	**50.93**	**61**	**1**	**49**	**0.88**	**0.13**	**3.34**	**1.11**	**-11.65**	**-87.19**	**234.50**	**11.28**
	STD	18.08	13.65	4.77	18.08	5.15	22.64	2.82	20.30	22.64	33	0	36	0.23	0.06	1.20	0.30	23.20	5.68	119.81	30.43
100 – 500 (n=9)	**Avg.**	**45.30**	**35.96**	**18.74**	**54.70**	**12.96**	**39.72**	**12.44**	**47.84**	**60.28**	**121**	**6**	**693**	**0.85**	**0.35**	**2.75**	**1.10**	**-15.02**	**-65.45**	**174.55**	**10.25**
	STD	12.35	13.93	6.13	12.35	5.69	15.93	7.64	15.95	15.93	50	3	414	0.25	0.18	1.08	0.17	25.09	17.74	108.05	17.16
1,500 – 3,500 (n=9)	**Avg.**	**50.48**	**33.27**	**16.24**	**49.52**	**18.56**	**50.63**	**18.28**	**31.09**	**49.37**	**215**	**14**	**2,506**	**1.01**	**0.52**	**1.92**	**1.03**	**1.12**	**-48.14**	**91.55**	**3.13**
	STD	17.36	13.58	5.87	17.36	6.88	18.47	9.69	13.91	18.47	116	5	653	0.21	0.18	0.40	0.25	20.62	18.19	39.65	25.37
3500 – 15,000 (n=9)	**Avg.**	**47.82**	**34.47**	**17.71**	**52.18**	**37.41**	**51.55**	**35.38**	**13.08**	**48.45**	**339**	**20**	**6,091**	**1.09**	**1.03**	**0.70**	**0.93**	**8.82**	**2.87**	**-29.67**	**-7.25**
	STD	11.78	9.83	3.89	11.78	14.22	12.64	11.87	9.98	12.64	89	7	2,821	0.13	0.20	0.42	0.12	13.48	20.49	41.78	12.49
15,000+ (n=9)	**Avg.**	**43.10**	**38.91**	**17.99**	**56.90**	**46.35**	**43.31**	**38.58**	**18.11**	**56.69**	**793**	**106**	**89,608**	**1.00**	**0.99**	**1.01**	**1.00**	**0.39**	**-0.83**	**1.07**	**-0.20**
	STD	14.05	9.66	4.96	14.05	11.11	14.56	10.64	5.64	14.56	247	59	65,211	0.09	0.10	0.20	0.10	9.33	10.06	19.88	9.51

Appendix B. Chapter 3 Supplemental Data

Table B.1. Field sample results from TGA for coal and non-coal mass fractions

Sample Name	Region	Location	Obs. CO_2 *TGA Dust Sample Size	Obs. CO_2 Mass	TGA Dust Sample Size	Coal Mass Fraction	Non-Coal Mass Fraction
			μg^2	μg	μg	(%)	(%)
A-5-C-MCE20	NA	Feeder	11.54	0.92	12.61	51	49
A-5-F-MCE45	NA	Feeder	1,013.94	4.94	205.10	75	25
A-6-H-PVC7	NA	Intake	0.12	0.01	9.35	29	71
A-5-H-MCE15	NA	Intake	3.50	0.48	7.26	21	79
A-5-MF-MCE25	NA	Production	22.01	0.56	39.21	68	32
A-6-MF-PVC11	NA	Production	4.40	1.40	3.15	12	88
A-6-B-PVC20	NA	Production	90.17	2.80	32.20	41	59
A-5-T-MCE30	NA	Return	12.55	0.29	43.24	39	61
A-6-T-PVC10	NA	Return	115.69	2.77	41.72	27	73
A-6-T-PVC9	NA	Return	17,979.46	70.41	255.35	9	91
A-5-R-MCE50	NA	Return	146,658.99	201.31	728.52	12	88
A-6-R-PVC3	NA	Return	8,377,659.00	1818.53	4606.82	2	98
A-6-R-PVC4	NA	Return	8,282,871.88	1627.22	5090.19	2	98
B-3-F-MCE100	CA	Feeder	3.40	0.30	11.48	49	51
B-4-F-MCE120	CA	Feeder	53.83	0.89	60.39	12	88
B-1-I-MCE10	CA	Intake	-0.05	-0.01	5.20	41	59
B-2-I-MCE35	CA	Intake	3.27	0.19	17.14	52	48
B-4-B-MCE115	CA	Production	-10.61	-0.34	31.15	96	4
B-1-M-MCE25	CA	Production	10.38	0.35	29.92	53	47
B-3-B-MCE90	CA	Production	26.93	0.87	30.91	2	98
B-1-B-MCE30	CA	Production	43.24	1.47	29.40	9	91
B-1-B-MCE40	CA	Production	92.77	2.10	44.28	43	57
B-3-M-MCE95	CA	Production	197.08	1.66	118.74	19	81
B-2-B-MCE70	CA	Production	13,165.74	16.92	778.25	8	92
B-2-B-MCE55	CA	Production	18,285.08	16.66	1097.56	6	94
B-3-R-MCE85	CA	Return	10.26	0.60	17.23	16	84
B-4-R-MCE110	CA	Return	22.09	0.81	27.29	41	59
B-1-R-MCE15	CA	Return	40.59	1.11	36.51	22	78
B-2-R-MCE45	CA	Return	260.62	1.83	142.65	2	98
C-7-F-MCE16	SCA	Feeder	17.56	2.37	7.39	81	19
C-7-F-PVC16	SCA	Feeder	62.27	1.82	34.17	35	65
C-8-F-PVC53	SCA	Feeder	51.88	1.36	38.02	12	88
C-7-I-PVC3	SCA	Intake	10.24	-0.35	-29.09	44	56
C-7-I-MCE2	SCA	Intake	65.34	1.19	54.82	54	46
C-7-B-PVC17	SCA	Production	7.82	0.56	13.98	11	89
C-7-B-PVC23	SCA	Production	5.60	0.77	7.26	64	36
C-7-B-MCE12	SCA	Production	19.77	0.95	20.71	44	56
C-7-B-MCE9	SCA	Production	49.16	1.40	35.22	39	61
C-8-B-MCE28	SCA	Production	168.24	2.08	81.00	15	85
C-8-M-MCE22	SCA	Production	878.34	5.22	168.37	27	73
C-8-B-PVC55	SCA	Production	1,217.19	12.87	94.56	3	97
C-7-R-MCE3	SCA	Return	135.91	2.92	46.61	30	70
C-7-R-MCE11	SCA	Return	225.96	4.03	56.05	17	83
C-7-R-PVC21	SCA	Return	7,960.04	47.20	168.64	3	97

Table B.2. Single factor ANOVA analysis of Appalachian coal mining regions for field samples

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
NA	12	3.758640417	0.31322	0.059214
CA	16	4.803324747	0.300208	0.067888
SCA	16	4.882769527	0.305173	0.052494

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.001164846	2	0.000582	0.009719	0.990331	3.225684
Within Groups	2.457082179	41	0.059929			
Total	2.458247025	43				

Table B.3. Single factor ANOVA analysis of sampling locations in all mines for field samples

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Feeder (F)	7	3.151824319	0.450261	0.076135
Intake (I)	6	2.406966725	0.401161	0.016931
Production (P)	18	5.662612834	0.31459	0.073438
Return (R)	13	2.223330814	0.171025	0.01918

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.438167029	3	0.146056	2.892077	0.047099	2.838745
Within Groups	2.020079996	40	0.050502			
Total	2.458247025	43				

Table B.4. T-Test with two-sample analysis assuming unequal variances for comparing sampling locations within the mine for field samples

	F	*I*
Mean	0.450261	0.401161
Variance	0.076135	0.016931
Observations	7	6
Hypothesized Mean Difference	0	
df	9	
t Stat	0.419511	
P(T<=t) one-tail	0.342339	
t Critical one-tail	1.833113	
P(T<=t) two-tail	0.684679	
t Critical two-tail	2.262157	

	F	*P*
Mean	0.450261	0.31459
Variance	0.076135	0.073438
Observations	7	18
Hypothesized Mean Difference	0	
df	11	
t Stat	1.109365	
P(T<=t) one-tail	0.145469	
t Critical one-tail	1.795885	
P(T<=t) two-tail	0.290937	
t Critical two-tail	2.200985	

	I	*P*
Mean	0.401161	0.31459
Variance	0.016931	0.073438
Observations	6	18
Hypothesized Mean Difference	0	
df	19	
t Stat	1.042065	
P(T<=t) one-tail	0.15523	
t Critical one-tail	1.729133	
P(T<=t) two-tail	0.310461	
t Critical two-tail	2.093024	

	I	*R*
Mean	0.401161	0.171025
Variance	0.016931	0.01918
Observations	6	13
Hypothesized Mean Difference	0	
df	10	
t Stat	3.51066	
P(T<=t) one-tail	0.002813	
t Critical one-tail	1.812461	
P(T<=t) two-tail	0.005625	
t Critical two-tail	2.228139	

	F	*R*
Mean	0.450261	0.171025
Variance	0.076135	0.01918
Observations	7	13
Hypothesized Mean Difference	0	
df	8	
t Stat	2.512492	
P(T<=t) one-tail	0.018115	
t Critical one-tail	1.859548	
P(T<=t) two-tail	0.03623	
t Critical two-tail	2.306004	

	P	*R*
Mean	0.31459	0.171025
Variance	0.073438	0.01918
Observations	18	13
Hypothesized Mean Difference	0	
df	27	
t Stat	1.926159	
P(T<=t) one-tail	0.032337	
t Critical one-tail	1.703288	
P(T<=t) two-tail	0.064673	
t Critical two-tail	2.051831	