Considerations for TGA of Respirable Coal Mine Dust Samples

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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 [1,2,3]. 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 [4]. 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 [4,5].

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 [6-8]. In some areas of this region, there appears to even be an increase in the incidence of CWP and silicosis [1,6-8]. 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 [3,6,7,9]. 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 [10]. 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) [1,10,11]. 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. [11]. 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 [10,12,13]. 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 [10]. 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) [10].

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 [12,14]. The pump is run at a flow rate of 1.7 L/min to mimic the rate of human respiration [12,14]; 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) [12,14,15], and the silica fraction is determined by infrared spectroscopy (IR) by either NIOSH Method 7603 or MSHA Method P7 [16,17]. 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 [16,17].

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 [10]. 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) [12,13,18-20]. 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 [1,5,7]. 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 [10,21], and a combination of size and chemistry may influence the relative reactivity of particles within the respiratory system [21,22]. 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 [17]. 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 [23]. Weight change is generally plotted as a function of temperature or time on a thermogram [23,24], 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) [23,25-28]. 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) [29-31]. TGA has also been used for rank classification of coal samples [30].

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 [29,30]. 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., loose 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 illustrates hypothetical thermograms for this general example.
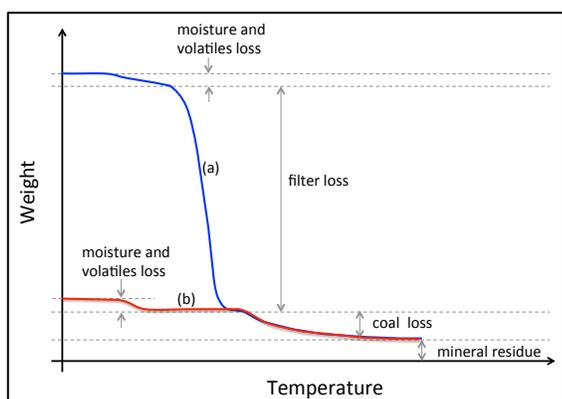

Fig. 1. Hypothetical thermograms for (a) direct-on-filter and (b) dust-only TGA of a respirable coal mine dust sample. For the direct-on-filter conceptualization, the filter media is assumed to decompose completely prior to coal oxidation.

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 [18,25-28]. 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 [32]. 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 [32]. 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) [16,17]. As illustrated in Figure 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 samples, we are using a Q500 Thermogravimetric Analyzer (TA Instruments, New Castle, DE). The Q500 employs a microbalance with $0.1\mu g$ resolution, and its vertical furnace eliminates some thermal influence on the balance [25,33]. 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 [34,35]. Table 1 provides a comparison of key characteristics, with favorable characteristics denoted by a star.

Table 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 [35]. MCE, on the other hand, is considered ashless and not susceptible to static buildup [34]. 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) [34].

3.1.2 Summary of Experiments and Results

To test the suitability of PVC and MCE filters (37 mm, $5\mu m$ pore size) for direct-on-filter TGA of respirable coal mine dust samples, preliminary experiments were conducted (see [36] 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 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., loosing 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.

Based on these observations, further experiments were run where raw coal was pulverized and collected onto PVC and MCE filters. Because the PVC filters are non-hygroscopic, the dust sample weight could easily be determined by weighing the filter before and after dust collection. A Sartorius Cubis Microbalance (Bohemia, NY) was used for this.).
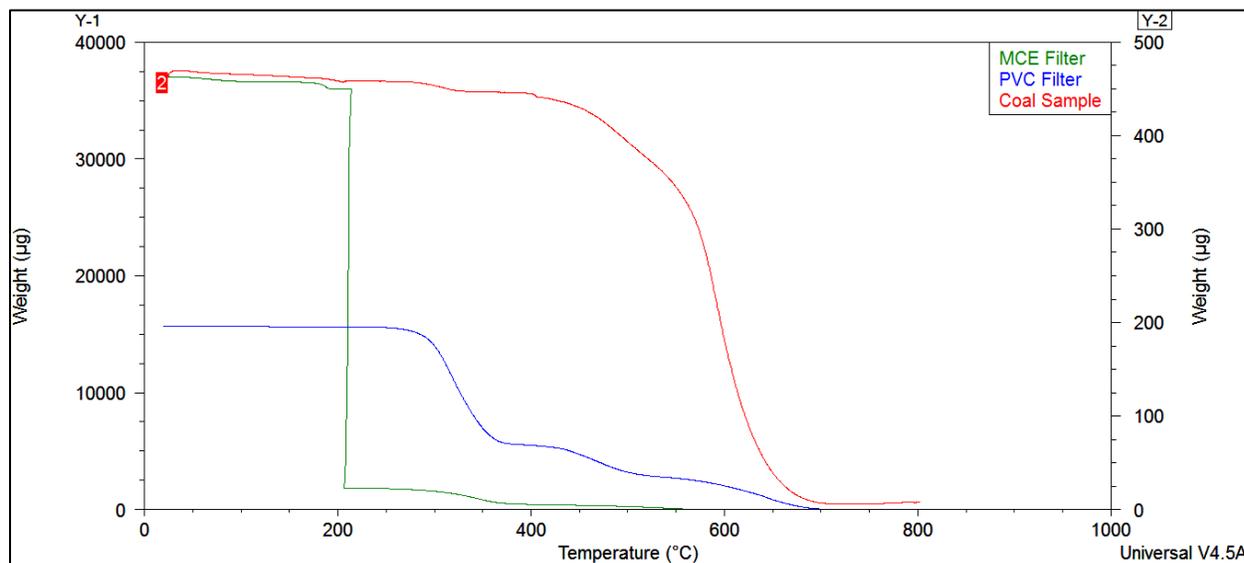

Fig. 2. Example thermograms for blank PVC and MCE filters (primary y-axis) and a raw coal sample (secondary y-axis). The PVC filter has two regions of weight loss, which span relatively wide temperature ranges, whereas the MCE filter losses most of its weight in one very narrow region. Coal oxidation 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 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 3.
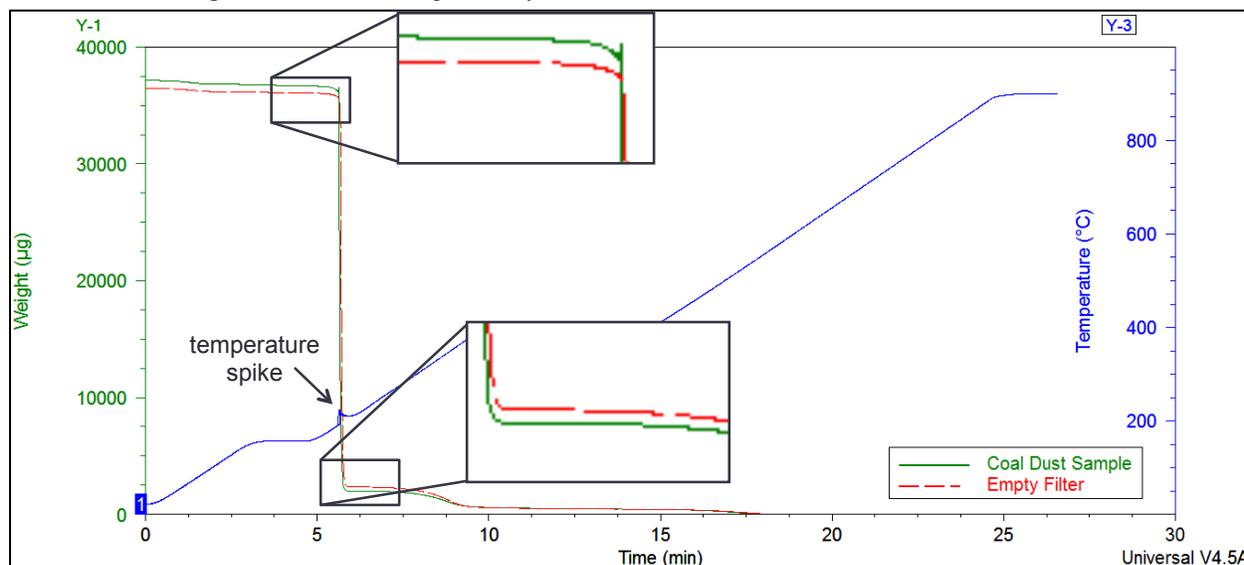

Fig. 3. Thermograms (weight on the primary y-axis vs. time) for a blank MCE filter and an MCE filter with dust generated from a raw coal sample; temperature is shown on the secondary y-axis. The difference in initial weights is about 80μg, with the dust-laden filter being heavier than the empty filter; 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 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 on the figure, there are four primary phases of sample weight change during the method.

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.
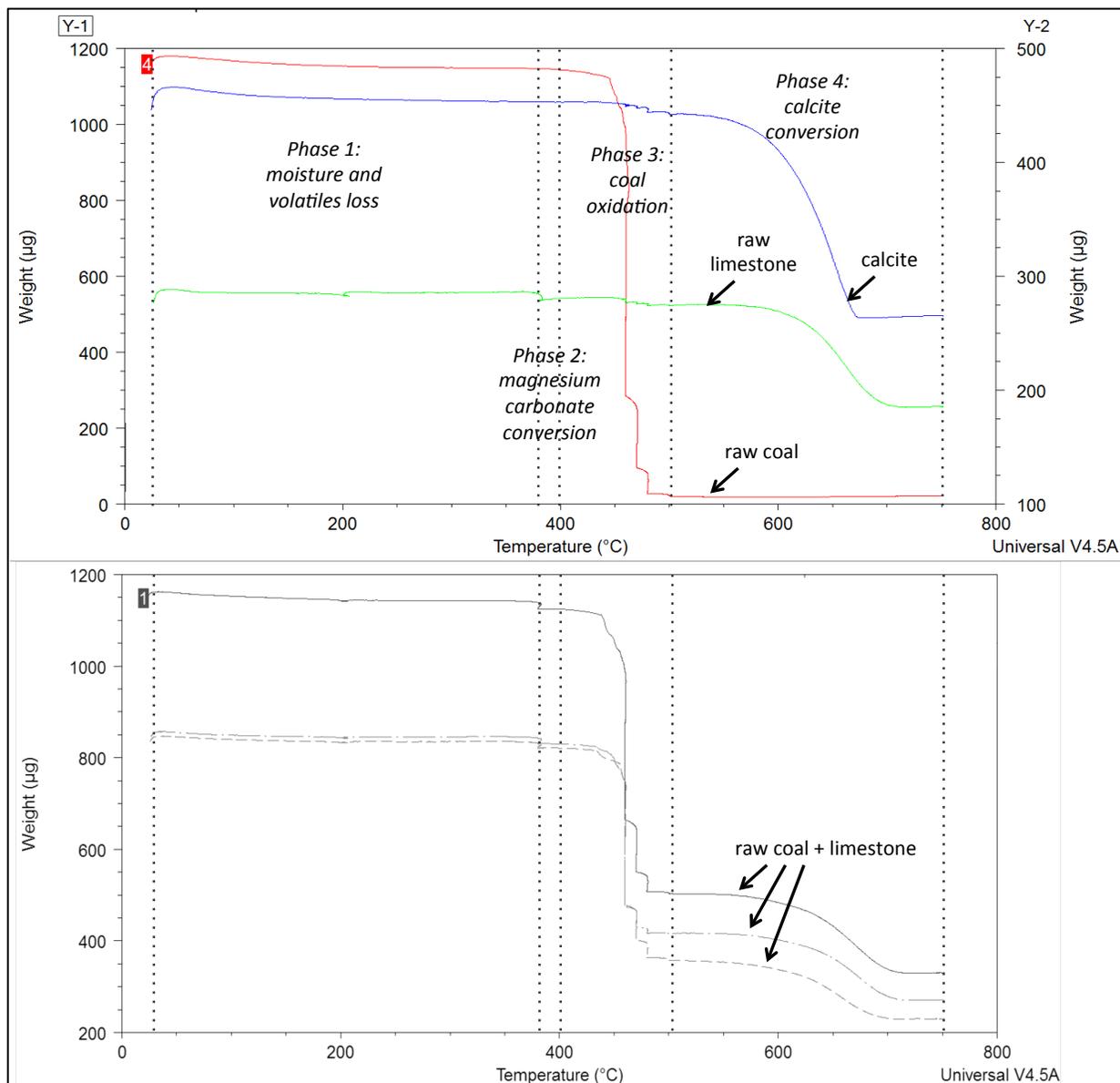
Fig. 4.Example thermograms for reagent grade calcite only, raw limestone only and raw coal dust only (top), and samples containing both raw coal and raw limestone dust (bottom). The TGA experiment method used here includes four major phases, which drive off moisture and volatiles at temperatures less 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.

References

[1] Suarthana, E., Laney, A. S., Storey, E., Hale, J. M., and Attfield, M. D. (2011). Coal workers' pneumoconiosis in

the United States: regional differences 40 years after implementation of the 1969 Federal Coal Mine Health and Safety Act. *Occupational and Environmental Medicine*, 68, 908-913.

[2] National Institute for Occupational Safety and Health (1974). Criteria for a Recommended Standard – Occupational Exposure to Respirable Coal Mine Dust. DHEW (NIOSH), Publication No. 95-106.

[3] World Health Organization. (1999). Hazard prevention and control in the work environment: airborne dust.

[4] US Environmental Protection Agency (USEPA). (2013). Particulate Matter (PM) Research. Retrieved from http://www.epa.gov/airscience/air-particulatematter.htm

[5] Castranova, V., and Vallyathan, V. (2000). Silicosis and coal workers' pneumoconiosis. *Environmental Health Perspectives*, *108*(Suppl 4), 675.

[6] Laney, A. S., and Attfield, M. D. (2010). Coal workers' pneumoconiosis and progressive massive fibrosis are increasingly more prevalent among workers in small underground coal mines in the United States. *Occupational and environmental medicine*, *67*(6), 428-431.

[7] Centers for Disease Control (CDC) (2006). Advanced Cases of Coal Workers' Pneumoconiosis-Two Counties, Virginia. MMWR, 55(33).

[8] dos S Antao, V. C., Petsonk, E. L., Sokolow, L. Z., Wolfe, A. L., Pinheiro, G. A., Hale, J. M., and Attfield, M. D. (2005). Rapidly progressive coal workers' pneumoconiosis in the United States: geographic clustering and other factors. *Occupational and environmental medicine*, *62*(10), 670-674.

[9] Schatzel, S. J. (2009). Identifying sources of respirable quartz and silica dust in underground coal mines in southern West Virginia, western Virginia, and eastern Kentucky. *International Journal of Coal Geology*, *78*(2), 110-118.

[10] Lowering Miners' Exposure to Respirable Coal Mine Dust, Including Continuous Personal Dust Monitors; Final Rule, 30 C.F.R. Parts 70, 71, 72, 75, and 90, (2014).

[11] Maintenance of Incombustible Content of Rock Dust in Underground Coal Mines; Final Rule, 30 C.F.R. Part 75, (2011).

[12] Colinet, J. F., Listak, J. M., Organiscak, J. A., Rider, J. P., and Wolfe, A. L. (2010). *Best practices for dust control in coal mining* (41-52). *DHHS*, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, Office of Mine Safety and Health Research.

[13] Reed, W. R., Listak, J. M., Page, S. J., and Organiscak, J. A. (2008). Summary of NIOSH Research Completed on Dust Control Methods for Surface and Underground Drilling. Trans Soc Min Metall Explor, *342*:32-40.

[14] Zefon. (2015). Coal Mine Dust Sampling System. Retrieved from http://www.zefon.com/analytical/download/Coal-Mine-Equipment.pdf

[15] Bartley, D. L., and Feldman, R. (1998). NIOSH Manual of Analytical Methods (NMAM), 4th Edition, Particulates Not Otherwise Regulated: Method 0600, Issue 3, 1-6.

[16] Schlecht, P., and Key-Schwartz, R. (2003). NIOSH Manual of Analytical Methods (NMAM), 4th Edition, QUARTZ in coal mine dust: Method 7603: Issue 3, 1-7.

[17] Mine Safety and Health Administration (MSHA) (2014). Infrared Determination of Quartz in Respirable Coal Mine Dust, Method No.: P-7. US Department of Labor, Retrieved from: http://www.msha.gov/Techsupp/pshtcweb/MSHA%20P7.pdf

[18] Sellaro, R. M. (2014). *Development and Demonstration of a Standard Methodology for Respirable Coal Mine Dust Characterization Using SEM-EDX*. Master's thesis, Virginia Polytechnic Institute and State University, Blacksburg, Virginia.

[19] Tuchman, D. P. (1992). Research toward direct analysis of quartz dust on filters using FTIR spectroscopy. US Department of the Interior, Bureau of Mines.

[20] Tuchman, D. P., Volkwein, J. C., and Vinson, R. P. (2008). Implementing infrared determination of quartz particulates on novel filters for a prototype dust monitor. *Journal of Environmental Monitoring*, *10*(5), 671-678.

[21] Mischler, Steven (2014) A Multistage Cyclone Array for the Collection of Size-segregated Silica Aerosols to Test the Hypothesis that Ultrafine Crystalline Silica Particles are More Efficient in Their Activation of Macrophages. Doctoral Dissertation, University of Pittsburgh.

[22] National Institute for Occupational Safety and Health (NIOSH). (1991). Work-related lung disease surveillance report. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, *DHHS,* (NIOSH) Publication No. 91–113, Table 23, p. 38.

[23] Coats, A. W., and Redfern, J. P. (1963). Thermogravimetric analysis. A review. Analyst, 88(1053), 906-924.

[24] TA Instruments. (2006). TGA: Thermogravimetric Analyzer: Q Series Getting Started Guide.

[25] Cheng, H., Liu, Q., Yang, J., and Frost, R. L. (2010). Thermogravimetric analysis of selected coal-bearing strata kaolinite. Thermochimica Acta, 507, 84-90.

[26] Mu, J., and Perlmutter, D. D. (1981). Thermal decomposition of carbonates, carboxylates, oxalates, acetates, formates, and hydroxides. *Thermochimica Acta*, *49*(2), 207-218.

[27] Hills, A. W. D. (1968). The mechanism of the thermal decomposition of calcium carbonate. *Chemical Engineering Science*, *23*(4), 297-320.

[28] Gabor, M., Toth, M., Kristof, J., and Komaromi-Hiller, G. (1995). Thermal behavior and decomposition of intercalated kaolinite. Clays and clay minerals, 43(2), 223-228.

[29] Annual Book of ASTM Standards (ASTM), Vol. 1994, Section 5, American Society of Testing Materials, Philadelphia, 1993, pp. D3172–D3189.

[30] Mayoral, M. C., Izquierdo, M. T., Andres, J. M., and Rubio, B. (2001). Different approaches to proximate analysis by thermogravimetry analysis. *Thermochimica Acta*, *370*(1), 91-97.

[31] Li, Q., Zhao, C., Chen, X., Wu, W., and Li, Y. (2009). Comparison of pulverized coal combustion in air and in O 2/CO 2 mixtures by thermo-gravimetric analysis. *Journal of Analytical and Applied Pyrolysis*, *85*(1), 521-528.

[32] Combustible Materials and Rock Dusting; Final Rule, 30 C.F.R. Part 75 Subpart E, (2011).

[33] Colinet, J. F. and Listak, J. M. (2012). Silica and Respirable Content in Rock Dust Samples. *Coal Age*.

[34] Danley, R.L. and Schaefer, J.W. (2008). System and Method for a Thermogravimetric Analyzer Having Improved Dynamic Weight Baseline. United States Patent Application Publication, 16 pages.

[35] Zefon. (2012). Material Safety Data Sheet: Nitocellulose Membrane Filters. http://www.zefon.com/analytical/download/MSDS%20-%20Zefon%20MCE%20Membrane%20Filters.pdf

[36] Zefon. (2015). *PVC Membrane Filters*. Retrieved from http://www.zefon.com/store/pvc-membrane-filter-gla-5000.html

[37] Keles, C., Scaggs, M., and Sarver, E., Preliminary Development of a TGA Method for Determining Coal to Mineral Ratios in Respirable Dust Samples, Proceedings of the 144th Annual Meeting and Exhibition of the Society of Mining, Metallurgy and Exploration Denver, CO February 15-18, 2015, preprints no. 15-137.