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Direct-on-Filter FTIR Spectroscopy to Estimate Calcite as A Proxy for Limestone ‘Rock Dust’ in Respirable Coal Mine Dust Samples

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Abstract: Application of fine, inert ‘rock dust’ (RD) to the surfaces in underground coal mines is a common method for mitigating coal dust explosion hazards. However, due to its size, RD has the potential to contribute to the respirable coal mine dust (RCMD) concentration. Though the RD component of RCMD does not appear to pose the sort of health hazards associated with other components such as crystalline silica, understanding its relative abundance may be quite helpful for evaluating and controlling primary dust sources. Given that RD products are frequently comprised of high-purity limestone (i.e., primarily calcite mineral), calcite may serve as a suitable proxy for measuring RD. To estimate the mass percentage of calcite in RCMD samples, this study demonstrates the successful application of direct-on-filter (DOF) Fourier-transform infrared (FTIR) spectroscopy. Incidentally, DOF FTIR has been the focus of recent efforts to enable rapid measurement of crystalline silica in RCMD. Concurrent measurement of other constituents such as calcite is thus a logical next step, which can allow a broader interpretation of dust composition and source contributions.

Keywords: rock dust; FTIR; respirable coal mine dust; calcite; RCMD; carbonates



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1. Introduction

Underground coal mining activities produce fine combustible coal dust. When present with methane—a gas naturally released from coal seams—there is a devastating risk of coal mine explosions [1,2]. It is well established that the use of inert ‘rock dust’ (RD) products can effectively prevent coal dust from taking part in such explosions [3]. During an explosion, the RD disperses, mixes with the coal dust, and prevents propagation of the flame front by acting as a heat sink [3,4].

The practice of RD application to coal mine surfaces dates back more than a century, and federal regulatory requirements for rock dusting in US mines were included in the Coal Mine Safety and Health Act (1969) [5]. The regulation covers both application practices and product specifications. Although a variety of materials might be used to generate RD (e.g., dolomite, gypsum, anhydrite, shale, adobe), most products are comprised of pulverized, high-purity limestone (i.e., natural calcite or calcium carbonate, CaCO_3) since it is inexpensive and widely available. In addition to being inert, RD products must also have relatively fine particle size to effectively mitigate coal dust explosion [6].

A joint survey by NIOSH and MSHA showed that there has been an increase in the fine coal dust in US coal mines over the past several decades, possibly due to an increase in mechanization [3]. Since finer coal dust has more surface area, it requires the application of more RD to inert [6]. This, along with an increased focus on limiting respirable coal mine dust (RCMD) exposure, has prompted questions regarding the contribution of RD to the overall RCMD concentration and the possible implications for occupational health [6,7].

While acute exposure to calcite dust has not been shown to induce significant cytotoxicity, respiratory irritation is possible, which might contribute to a higher risk of chronic

obstructive pulmonary disease (COPD) [7–9]. That said, whenever health effects due to RD products have been reported, the respirable crystalline silica (RCS) content was proposed to be the most likely cause [9]. It is noted that United States regulation does allow for a small percentage of respirable crystalline silica (RCS) in RD products ($\leq 4\%$ by mass, per 30CFR §75.2), but studies have consistently indicated that common products typically do not exceed the standard [7,10–12].

Still, if RD is significantly contributing to the RCMD concentration, this information is important to the overall understanding of dust sources and possible risks. For example, given equal exposure concentration and time, RCMD that is mostly sourced from limestone RD application likely presents less risk than RCMD that is mostly sourced from drilling into high-silica roof rock. Several recent studies have indicated that RD can indeed contribute to the RCMD concentration in some locations of underground mines [11,13–17]. These studies have relied on analytical methods such as scanning electron microscopy with energy dispersive X-ray (SEM-EDX) or thermogravimetric analysis (TGA) to investigate RCMD components. While valuable for research, such methods are simply not feasible for routine mine monitoring. Rather, methods are needed that can provide quick data on key RCMD components—enabling interpretation of dust sources and timely decision-making on interventions [7].

A direct-on-filter (DOF) method that uses Fourier Transform Infrared (FTIR) Transmission Spectroscopy has been in development by the US National Institute for Occupational Safety and Health (NIOSH) for the measurement of RCS in RCMD samples [18–20]. Miller et al. showed a strong linear correlation (R-squared value of 0.90–0.97) between the DOF method and the standard MSHA P7 method for RCS analysis [18]. In addition to RCS, though, this method can be used to estimate other minerals captured by the infrared spectra. Stach et al. combined data from transmission and diffuse reflectance infrared spectroscopy into a unified calibration model to estimate different minerals (such as alpha quartz, dolomite, and calcite) in real-world and lab-generated samples, expanding upon the current techniques that determine only alpha quartz [21]. The potential to estimate kaolinite as a co-indicator of rock strata sourced dust (along with RCS) has recently been investigated [22].

The current work aims to demonstrate the potential of the DOF FTIR method for estimating calcite as a proxy for RD in RCMD samples. To this end, RCMD samples from various locations in 16 underground mines were analyzed, along with laboratory-generated samples of respirable dust from primary source materials (e.g., RD products, raw coal, and rock strata) obtained from 15 of the 16 mines. The FTIR-derived calcite results are compared to estimations of the carbonate mineral fraction derived from TGA and SEM-EDX.

2. Materials and Methods

A total of 93 sets of RCMD samples were collected from 16 underground coal mines in the United States (numbered as Mines 10–25, see Table 1). The sample sets were collected in key locations where RCMD source contributions were expected to vary based on nearby activities (Table 2); while an effort was made to sample all five locations in each mine, this was not always possible. Each set contained multiple samples that were collected simultaneously for about 2–4 h.

All sampling equipment and materials were obtained from Zefon International (Ocala, FL, USA). Sampling trains included a 10-mm nylon Dorr-Oliver cyclone and Escort ELF air pump (operated at 2.0 L/min to collect the respirable fraction of the airborne dust) to collect dust directly onto a 37-mm filter housed in a two-piece styrene cassette. In each sample set, at least three samples were collected: one on a polyvinyl chloride (PVC) filter (5.0- μm pore size), and two on polycarbonate (PC) filters (track-etched with 0.4- μm pore size). The PVC filters were used for the DOF FTIR analysis and were pre- and post-weighed to determine the total sample mass using a microbalance (Sartorius MSE6.6S, Gottingen, Germany); the PC filters were used for TGA and SEM-EDX as described later.

Table 1. Number and location of RCMD sample sets and dust source materials collected in the 16 underground coal mines included in this study. Descriptions of sampling locations are provided in Table 2.

Mine Number	Mining Method ¹	RCMD Sample Sets					Dust Source Materials					
		Sampling Location ²					RCMD Total	Material ³				Source Material Total
		I	B	F	P	R		RD	C	RS	BD	
10	RP	1	2	2	2	1	8	-	-	1	1	2
11	RP	-	1	1	1	1	4	1	-	1	-	2
12	RP	1	1	-	1	1	4	1	1	1	-	3
13	LW	2	1	1	-	2	6	1	1	-	1	3
14	RP	1	1	1	1	-	4	1	1	1	1	4
15	RP	1	1	1	1	1	5	1	1	1	-	3
16	RP	-	1	1	1	1	4	1	1	-	1	3
17	LW	2	1	-	1	2	6	1	1	-	1	3
18	RP	1	1	1	1	1	5	1	1	1	1	4
19	RP	1	1	1	1	2	6	1	1	1	1	4
20	RP	1	1	2	1	1	6	1	-	-	1	2
21	RP	1	1	1	1	1	5	-	1	1	1	3
22	RP	1	-	1	1	-	3	1	1	1	1	4
23	LW	3	-	-	2	1	6	1	1	1	1	4
24	LW	3	-	1	-	2	6	1	-	-	1	2
25	RP	1	1	1	8	4	15	-	-	-	-	0
Total		20	14	15	23	21	93	13	11	10	12	46

¹ RP: Room and pillar method with continuous miner; LW: Longwall method. ² I: Intake; B: Roof bolter; F: Feeder; P: Production; R: Return

³ RD: Rock dust; C: coal; RS: rock strata; BD: bolter dust.

Table 2. Description of the five key sampling locations within each mine.

Location	Description
Intake (I)	In the fresh airways, upstream of any bolting or mining activities
Roof bolter (B)	Just downwind of an active roof bolter
Feeder (F)	Adjacent to the feeder breaker, or along the main conveyor belt or transfer points
Production (P)	Just downwind of an active continuous miner, or on the longwall face
Return (R)	In the exhaust airway, including downwind of ventilation tubing exhaust where present

At the time of RCMD sampling, bulk samples of primary dust source materials were also collected from 15 of the mines (Table 1). These include: the RD product being applied in the mine; run-of-mine coal (C) and rock strata (RS) materials that were pulled from the production belt; and material pulled from the roof bolter dust collection system (BD). In total, 46 source materials were collected, and these were used to generate respirable dust samples in the lab.

Since the bulk C and RS materials were very coarse (usually +5 μm), they were first pulverized and sieved to -230 mesh ($-63 \mu\text{m}$) to create a powder from which the respirable particles could be sampled; the RD and BD materials were already quite fine and required no preparation. To collect respirable dust from each source material, a small mass of the powdered material was aerosolized in a sealed enclosure using compressed air. The aforementioned sampling trains were used to collect samples (three on PVC filters and three on PC for each material) over durations of several minutes. Again, the PVC filters were pre- and post-weighed to determine the total sample mass.

2.1. Fourier Transform Infrared (FTIR) Analysis and Calibration

All available PVC filters (RCMD and lab-generated samples of dust source materials) were analyzed using a portable FTIR transmission instrument (ALPHA II, Bruker, Billerica, MA, USA). For this, the filter was carefully placed into a compatible four-piece cassette (Zefon International; Ocala, FL, USA), which was mounted onto a sample cradle and placed inside the instrument compartment so that the IR beam passed through the center of the filter [23]. The absorbance spectrum was obtained from 16 scans of the central 6-mm diameter area of each filter at a resolution of 4 cm^{-1} in the spectral range of 4000 cm^{-1} to 400 cm^{-1} , using Blackman-Harris three-term apodization function. Raw spectra were then background corrected using Bruker's OPUS software (Version 8.2.28, 32 bit). The correction

was done by subtracting the spectra of a blank PVC filter from that of the dust sample filter. A rubber band baseline correction with 64 baseline points was performed on the resultant spectra to remove distortions [18,24].

To determine calcite mass (μg) from a sample's FTIR spectra, a quantification model was developed using lab-generated samples of respirable sized particles of pure and natural calcite (CB Minerals LLC, Mamaroneck, NY, USA). A total of eight samples (~ 100 – $1200 \mu\text{g}$) were prepared on pre- and post-weighed PVC filters using the same procedure as for the powdered mine dust source materials and then analyzed by FTIR as described above. In the IR spectra of pure calcite, one of its major characteristic peaks appears at $\sim 877 \text{ cm}^{-1}$ [25]. The OPUS software was used to calculate the integrated absorbance peak area in the spectral range of 890 to 865 cm^{-1} , which can be correlated to the calcite sample mass. Figure 1 shows the results for the pure calcite samples and supports a linear correlation between the integrated FTIR peak area and calcite mass (Equation (1)):

$$\text{Calcite mass } (\mu\text{g}) = \frac{\text{Absorbance peak area}}{0.00334} \quad (1)$$

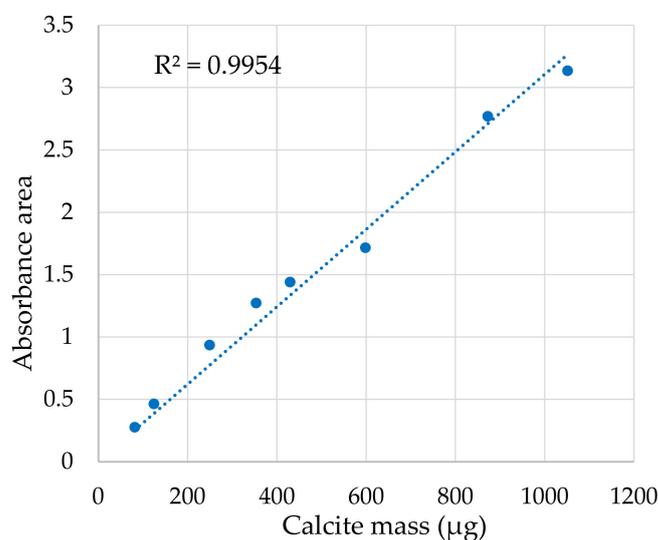


Figure 1. Calibration curve for the calcite quantification model prepared using eight respirable samples of respirable pure calcite. The Y-axis shows the integrated absorbance peak area for calcite (between 890 to 865 cm^{-1}) as a function of sample mass (μg) determined gravimetrically.

Following the collection of the FTIR spectra, Equation (1) was used to estimate the calcite mass (μg) in the lab-generated samples of dust source materials. Then, calcite mass was converted to calcite mass fraction (%) using the total dust sample mass. As mentioned, multiple PVC filters were collected for each source material, so the reported calcite results represent their average.

To estimate calcite mass in the RCMD samples, Equation (1) was slightly modified. This is because, unlike the lab-generated samples of dust source materials and pure calcite, the RCMD samples were collected in relatively low-concentration environments (and over longer sampling duration), which can affect the dust deposition pattern on the PVC filter—i.e., samples collected in high-concentration environments tend to have more center-heavy loading, which can slightly change the relationship between FTIR calcite peak area measured on the center of the filter and total calcite mass across the entire filter area. As such, Equation (1) was modified to Equation (2):

$$\text{Calcite mass } (\mu\text{g}) = \frac{F_{lab}}{F_{RCMD}} \times \frac{\text{Absorbance peak area}}{0.00334} \quad (2)$$

where $\frac{F_{lab}}{F_{RCMD}}$ is the ratio of the calibration factors determined for RCS in sampling environments representative of the lab sampling conducted in the current study and RCMD sampling. $F_{RCMD} = 0.00465$ and was previously established by NIOSH using pure quartz calibration samples collected in a calm air dust chamber with low concentration [19]. $F_{lab} = 0.00695$ and was developed by the authors of the current study using a similar quartz material as NIOSH, but the samples were collected in the same manner and high concentration enclosure described above for pure calcite and mine dust source materials.

For the FTIR instrument used here, the limits of detection (LOD) and quantification (LOQ) for calcite were estimated to be $\sim 1 \mu\text{g}$ and $\sim 3 \mu\text{g}$, respectively, using the standard deviation of the calcite peak measurement of 20 blank PVC filters.

2.2. Thermogravimetric Analysis (TGA)

TGA was used to analyze one PC filter from each of the 93 RCMD and 46 lab-generated sample sets. TGA is a mass-based method that can be used to estimate the coal, carbonate, and non-carbonate mineral fractions in a dust sample, and these fractions can be loosely correlated with the primary dust sources in many coal mines (i.e., the coal strata, RD products, and rock strata, respectively). The TGA method has been described in detail by Agioutanti et al. [26]. Briefly, the dust was recovered from the PC filters by sonication in isopropyl alcohol, transferred to a clean tared pan, and analyzed by a Q500 Thermogravimetric Analyzer (TA Instruments, New Castle, DE, USA) using a specified thermal ramping routine. The TGA routine proceeds as follows: ramp from ambient to 200 °C (50 °C/min) and isotherm at 200 °C for 5 min; ramp to 480 °C (20 °C/min) and isotherm for 50 min; ramp to 800 °C (20 °C/min) and isotherm for 5 min. Based on the work by Agioutanti et al., the coal is expected to completely oxidize between 200 and 480 °C, and carbonates (modeled as calcite) should thermally decompose between 400 and 800 °C ($\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$) [27]. Thus, the sample residue at the end of the TGA routine is assumed to be CaO + noncarbonate minerals. Then, a series of mass balance equations established by Agioutanti et al. was applied to apportion the dust to the three fractions specified above using the sample weight change in a few characteristic temperature regions [26]. It is noted here that the TGA method was developed using similar sample sizes as the RCMD and dust source material samples analyzed for this study.

2.3. Scanning Electron Microscopy with Energy Dispersive X-ray (SEM-EDX)

One PC filter from each of the 93 RCMD and 46 lab-generated sample sets was also analyzed by SEM-EDX, which yielded data on particle size and mineralogy distributions. Sample preparation and analysis were done following the methods outlined by Sarver et al. [13]. Briefly, a 9-mm sub-section was carefully cut from each filter and sputter coated with Au/Pd. Then, it was analyzed using an FEI Quanta 600 FEG environmental SEM (Hillsboro, OR, USA) equipped with a backscatter electron detector BSD and a Bruker Quantax 400 EDX spectroscope (Ewing, NJ, USA). The analysis covered particles in the range of about 0.1–10 μm and included about 800 particles per sample.

Each particle's long and intermediate (perpendicular to long) dimensions were measured, and its elemental spectra were used to bin it into one of eight mineralogy classes per Table 3 or into an "other" class if it did not meet the criteria for one of the defined classes. Of relevance to the current study, the carbonate class (CB) is expected to be dominated by RD-sourced particles in many coal mines; the other classes are expected to contain coal (C, MC) and non-carbonate mineral particles (e.g., ASK, ASO, S) primarily sourced from cutting or drilling into the coal and surrounding rock strata, and possibly diesel particulates (included in C) in some mines [13,28]. Particle dimensions and classifications were used to estimate the mass fraction of dust in each class. This was done by first computing each particle's volume using the product of its projected area diameter and short dimension, based on an assumed ratio for the short-to-intermediate (S:I) dimension for each mineralogy class (i.e., where the short dimension is the height of the particle as it sits on the filter; Table 3). Then, the volume was multiplied by an assumed specific gravity, again based on

the mineralogy class (Table 3). Finally, the computed particle masses were summed for each of the classes and divided by the total mass of particles in all classes for the sample.

Table 3. SEM-EDX classification criteria for sub- and supra-micron particles, along with assumptions for S:I ratio and SG for each mineralogy class (updated from Sarver et al. [13]).

Class ¹	Routine	Normalized Atomic % by Element								Particle Size to Mass Assumptions	
		C	O	Al	Si	Ca	Mg	Ti	Fe	S:I	SG
C	Sub Supra	≥75	<29	≤0.30	≤0.30	≤0.41	≤0.50	≤0.50 ≤0.06	≤0.50 ≤0.15	0.6	1.4
MC	Sub Supra			<0.44 <0.35	<0.44 <0.35	≤1.00 ≤0.50	≤0.50 ≤0.50	≤1.00 ≤0.60	≤1.00 ≤0.60	0.6	1.4
ASK ²	Sub			≥0.44, (≥37)	≥0.44, (≥42)	(<16)	(<4)	(<8)	(<10)	0.4	2.6
	Supra			≥0.35, (≥39)	≥0.35, (≥32)	(<8)	(<15)	(<13)	(<13)		
ASO ²	Sub			≥0.44, (≥37)	≥0.44, (≥42)	(≥16)	(≥4)	(≥8)	(≥10)	0.4	2.6
	Supra			≥0.35, (≥39)	≥0.35, (≥32)	(≥8)	(≥15)	(≥13)	(≥13)		
SLO ³	Sub				≥0.50					0.4	2.6
	Supra				≥0.33						
S ⁴	Sub				≥0.50					0.7	2.65
	Supra				≥0.33						
M	Sub Supra			>1.00				>1.00	>1.00	0.7	4.96
CB	Sub Supra	<88	>9			>1.00 >0.50	>0.50			0.7	2.7

¹ C: carbonaceous; MC: mixed carbonaceous; ASK: aluminosilicate-kaolinite; ASO: aluminosilicate-other; SLO: silicates-other; S: silica; M: heavy minerals; CB: carbonates. ² To differentiate ASK from ASO, additional limits for Al, Si, Ca, Mg, Ti, and Fe are shown in parenthesis (normalized to exclude C and O) ³ Additional limits for SLO: Si/(Al + Si + Ca + Mg + Ti + Fe) < 0.5. ⁴ Additional limits for S: Al/Si < 1/3 and Si/(Al + Si + Ca + Mg + Ti + Fe) ≥ 0.5.

3. Results and Discussion

3.1. Dust Source Materials

As a proof-of-concept, Figure 2 presents results on the lab-generated respirable samples from all 46 dust source materials. Data are available in Table S1 in the Supplementary Materials. As expected, all but one of the 13 RD material samples show very high fractions (>90%) of calcite per the FTIR analysis. These results are validated by the TGA- and SEM-EDX-derived carbonate mass fractions (Figures 2a and 2b, respectively), and the good agreement between all three methods suggests that most of the carbonate content in the samples is indeed calcite. For the one sample that shows only about 63% calcite, the higher TGA and SEM-EDX carbonate estimations (95% and 98%, respectively) indicate that this RD product also contained significant dolomite content (and indeed a significant peak corresponding to dolomite was observed on the FTIR spectra, though not quantified).

Notably, for two of the RD material samples, the FTIR actually indicates calcite mass fraction greater than 100%, which is practically impossible. This is likely due to particularly center-heavy dust loading on the filter samples generated for these two materials. As previously mentioned, the dust deposition pattern on the sample filter can influence the FTIR result; and while the sample collection procedure was the same for all lab-generated samples, it is possible that these RD materials had a slightly increased tendency for center loading relative to the pure and fine calcite samples used for calibration (Figure 1). For example, this could happen if the particle size distribution was relatively coarse. Nevertheless, even with some overestimation of the calcite % in these two materials, the FTIR results are still in good agreement with the TGA and SEM-EDX (i.e., absolute difference of <11% in ~90% of sample pairs, with mean differences of ±7.3% and ±3.4%, respectively).

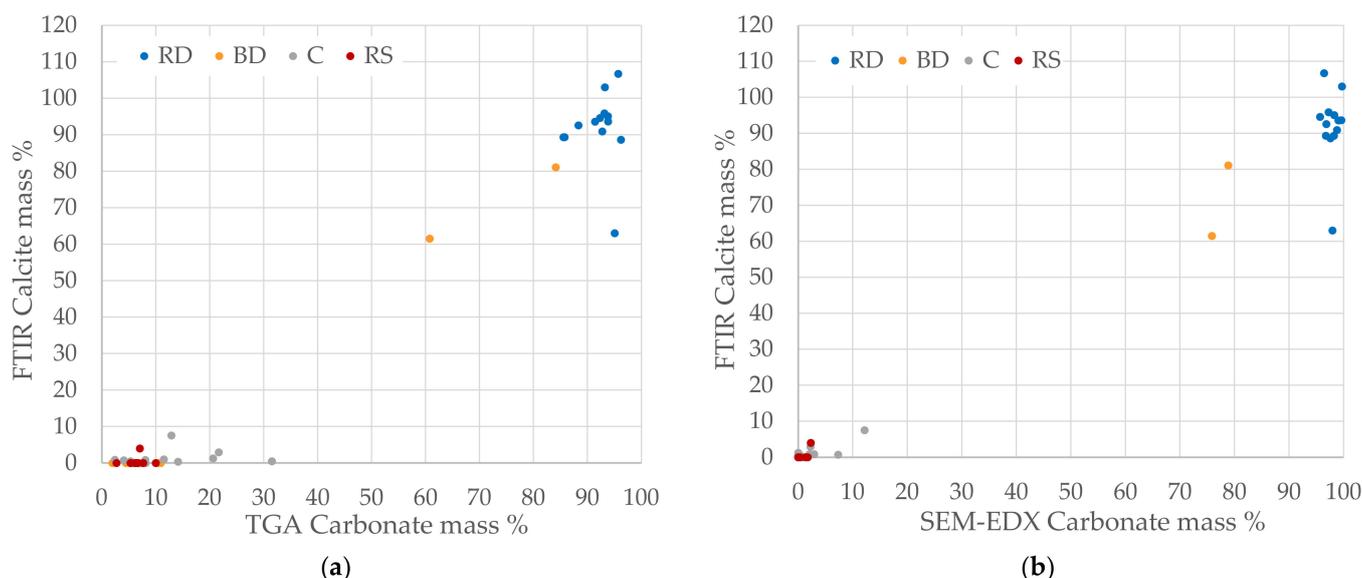


Figure 2. Comparison of FTIR-derived calcite % and (a) TGA- or (b) SEM-EDX-derived carbonate % for lab-generated respirable dust samples from RD, BD, C, and RS source materials ($n = 46$ each). In total, none of the 13 RD samples; 10 of the 12 BD samples; 1 of the 11 C samples; and 9 of the 10 RS samples had calcite mass less than LOD for the FTIR; none of the samples had calcite mass between LOD and LOQ.

For the other dust source materials, the FTIR results were also generally consistent with expectations (and the TGA and SEM-EDX results), with most of the C, RS, and BD samples showing very low calcite fractions. In fact, for many samples, the FTIR result was below the LOD or LOQ. Two BD samples (Mines 19 and 20) did show high calcite content (62% and 81%, respectively). This is attributed to the fact that the roof rock in these mines is characterized as limestone, whereas all other mines represented in this study had primarily shale, sandstone, and/or slate roof rock strata. Thus, while the calcite (or carbonate) fraction of RCMD is generally expected to be associated with RD application in the mine, exceptions are certainly possible.

It should also be mentioned that the TGA indicated significant carbonate content (>20%) in a few C material samples (Mines 13, 15, and 21), which disagreed with the corresponding FTIR and SEM-EDX results. However, upon inspection of the thermograms for those samples it was observed that the coal did not completely oxidize in the expected temperature range as it does for most coal materials—so the TGA method misclassified some coal as carbonates.

3.2. RCMD

Figure 3 presents the results for the RCMD samples (and data are tabulated in Table S2). Again, comparisons are shown between the FTIR-derived calcite and the TGA- and SEM-EDX-derived carbonate fractions (Figures 3a and 3b, respectively). Overall, the results from the three methods generally trend together, though there is a lot of scatter in the data. Moreover, while the FTIR tends to overpredict the TGA, it tends to underpredict the SEM-EDX. Both of these observations can be attributed, at least in part, to the relatively low masses of many of the available RCMD samples. Of the 93 samples on PVC filters (i.e., on which the dust mass could be accurately weighed), 51 had a mass <200 μg ; and on 8 samples the mass was insufficient to conduct FTIR and/or TGA (i.e., $n = 85$ in Figure 3).

Figure 4 illustrates, as a function of RCMD sample mass, the relative agreement between the FTIR and TGA or SEM-EDX results. For this plot, the ordinate (y) axis values represent the difference between FTIR calcite %—TGA or SEM-EDX carbonate % (e.g., for a sample that showed 23% calcite by FTIR and 17% carbonate by TGA, the plot shows $23\% - 17\% = 6\%$). There is much better agreement between the methods with increasing samples mass, which makes sense considering that the accuracy of both FTIR and TGA

is mass-limited. For samples with mass >200 μg , the mean difference observed between the FTIR—TGA and FTIR—SEM-EDX results is just $\pm 6.1\%$ and $\pm 3.4\%$, respectively. For relatively low mass samples, however, the over/underprediction trends in Figure 3 become clearer. All that said, it is worth noting that the RCMD samples included in this study have generally lower masses (due to short sampling times) than would be expected for full-shift RCMD samples (i.e., similar to what might be collected for the DOF-FTIR analysis of RCS that has been proposed by NIOSH).

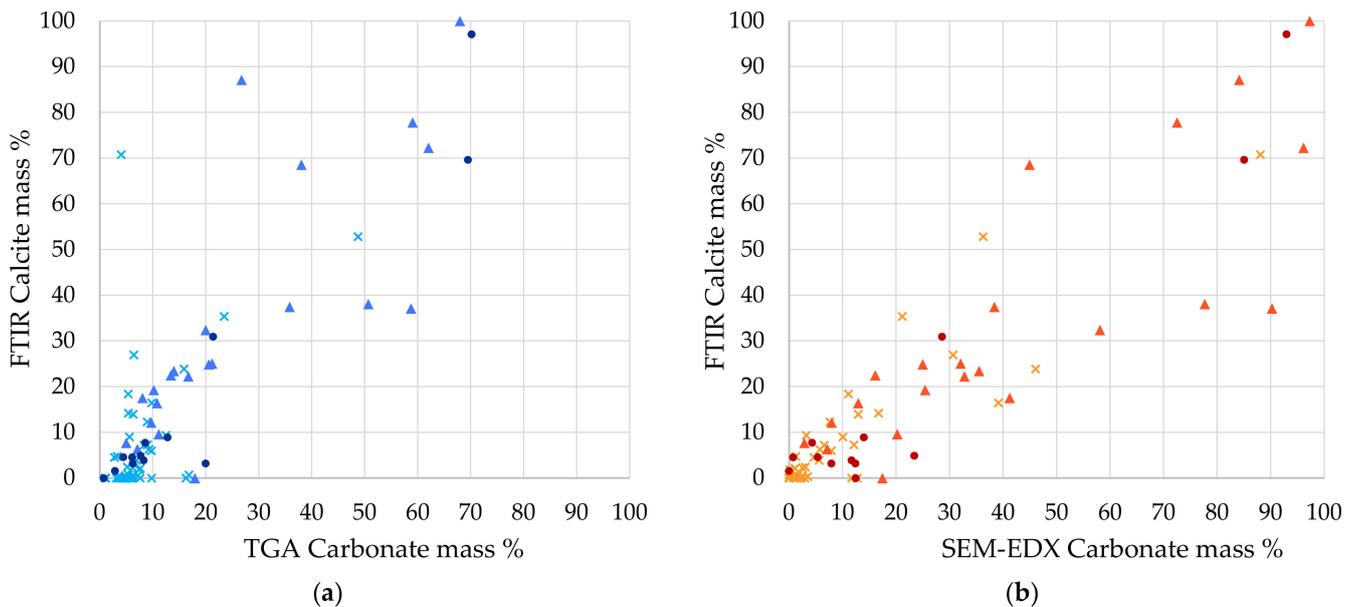


Figure 3. Comparison of FTIR-based calcite mass % and (a) TGA- or (b) SEM-EDX-based carbonate mineral mass % versus on corresponding PC and PVC filters from each sample set ($n = 85$ each). In the figures, \times = FTIR calcite mass below LOD, \blacktriangle = between LOD and LOQ; \bullet = above LOQ. In total, 37 of the 93 FTIR samples had calcite mass below the LOD, 28 samples were between LOD and LOQ, and 28 samples were above LOQ.

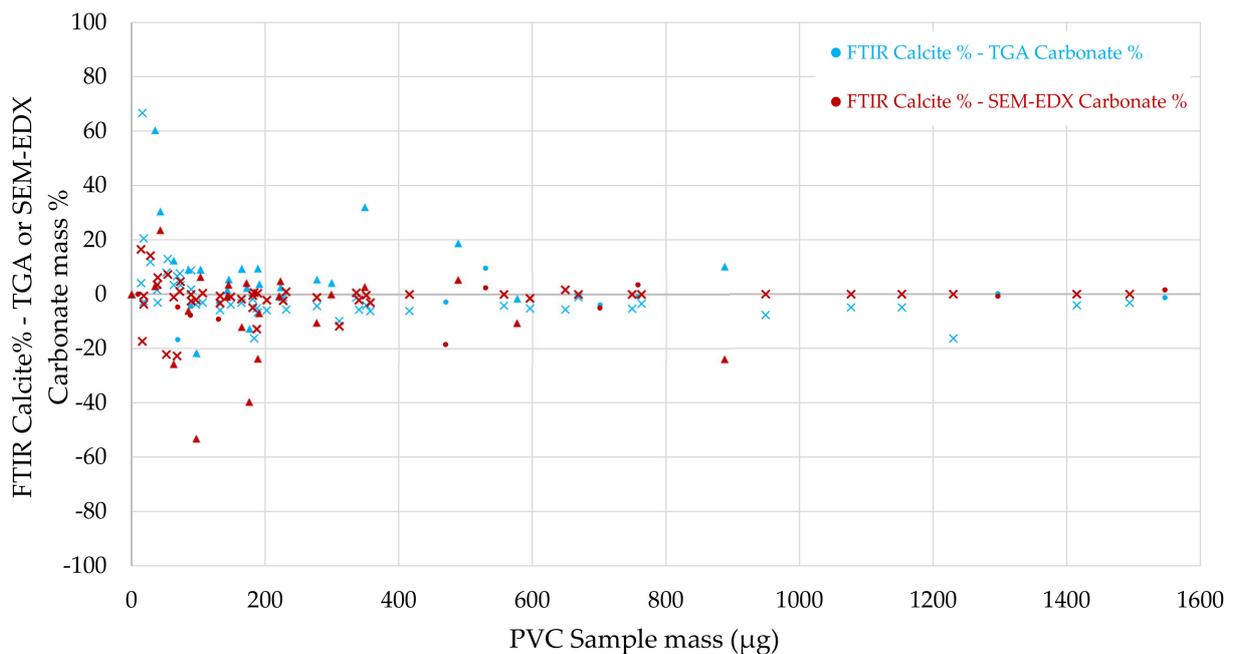


Figure 4. Difference between FTIR-based calcite mass % and TGA- or SEM-EDX-based carbonate mineral mass % versus sample mass on each PVC replicate sample collected in US underground coal mines ($n = 85$ for both). \times = FTIR calcite mass below LOD, \blacktriangle = between LOD and LOQ; \bullet = above LOQ.

Figure 5 presents the FTIR, TGA, and SEM-EDX results with respect to the specific RCMD sampling locations. Note that results from Mines 19 and 20 are excluded from the figure since limestone roof strata in these mines confounds the use of calcite/carbonate as a proxy for RD contribution to the RCMD. The relatively wide discrepancies between results for intake and feeder samples are attributed to the typically low sample masses in these locations (18 out of 20 intake and 13 out of 15 feeder samples were $<200 \mu\text{g}$).

Both the FTIR and SEM-EDX suggest that RD contributes significantly to the RCMD in many intake samples. This is consistent with expectations since rock dusting is routinely performed in intake airways, which are also upwind of most other activities (e.g., roof bolting, coal/rock extraction, and crushing/handling that generate dust from the geologic strata in the mine) aside from traffic that can re-entrain dust. Results from all three methods additionally indicate that RD can sometimes contribute significantly to RCMD in the return airways. This is logical since the returns receive dust transported from all other airways in the mine, and these areas themselves may undergo further rock dusting.

On the other hand, the RD contribution to RCMD generally appears to be minor in the roof bolter, production, and feeder locations, which are expected to be more influenced by nearby activities that generate dust from the mine strata. Notable exceptions were the roof bolter sample from Mine 17 and the production sample from Mine 23, which show relatively high calcite/carbonate fractions across all three analytical methods. Given that only the RD materials from these mines showed high calcite/carbonate, the results suggest that rock dusting upwind of the sampling locations did indeed contribute significantly to the RCMD. Indeed, extensive RD application was observed in the Mine 23 intake airway just upwind of the production face during the collection of the production and return samples, which showed $\sim 89\%$ and $\sim 63\%$ calcite, respectively. The intake sample in Mine 23 was collected during an earlier shift when active RD application was not observed, and it showed only $\sim 33\%$ calcite.

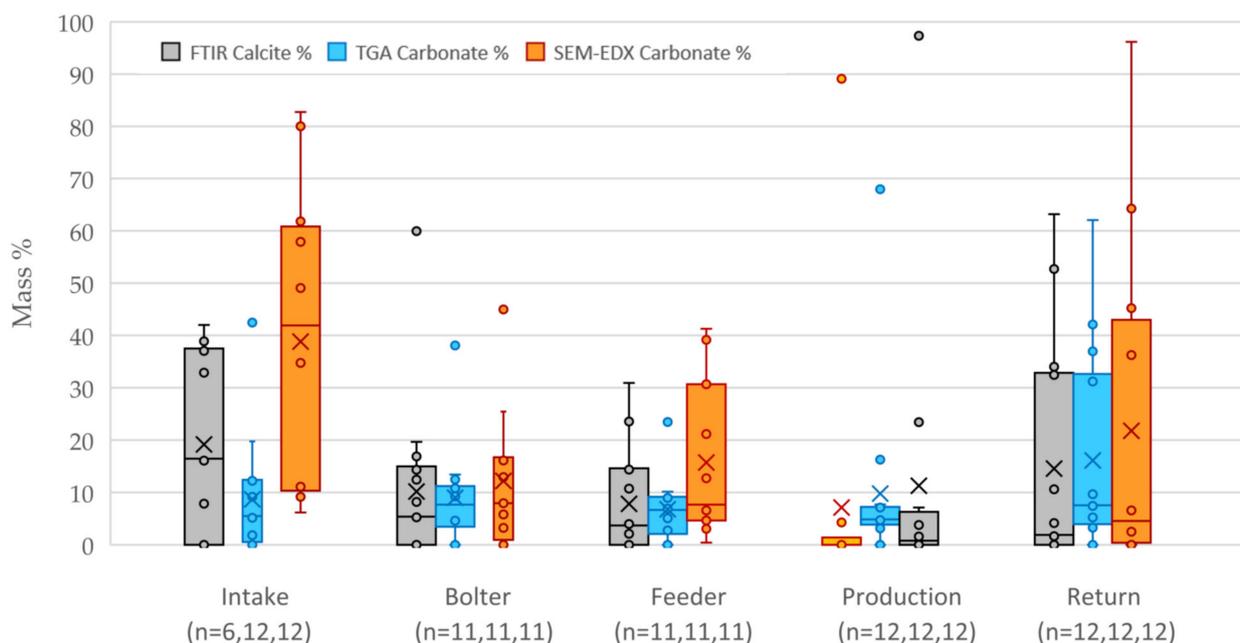


Figure 5. Box and whisker plot showing the FTIR, TGA, and SEM-EDX derived calcite/carbonate mass % for RCMD samples collected in each sampling location (excluding samples from Mines 19 and 20). In some mines, multiple sample sets were collected in a particular location (see Table 1); to avoid biasing results toward these mines, the multiple sample values were averaged to yield a single mine \times location value. Thus, n values show the number of data points available for each unique sampling location. Lower, middle, and upper box boundaries show the 25th, 50th, and 75th quartiles, respectively; lower and upper whisker lines show the lowest and highest values, respectively—except the outliers (defined as points 1.5 times the interquartile range away from the box boundaries); circles show the individual data points, and \times marks the mean calcite/carbonate mass %.

While active rock dusting was not always observed during RCMD sampling, the general appearance of mine floors and ribs provided anecdotal evidence that the larger longwall mines (as opposed to smaller mines using room and pillar methods with continuous miners) represented in this study were more frequently and extensively rock dusted. Accordingly, the RCMD samples collected in these mines tended to show higher calcite/carbonate content across all sampling locations (Table 4). This is especially evident for the production and return locations. Although generalization of these results is not advisable due to the relatively small number of longwall mine samples included in this study, it can be noted that the longwalls represented here were observed to have particularly effective dust controls at the production face (i.e., ventilation, water sprays on the longwall shearer that minimized RCMD from the coal/roof rock extraction).

Table 4. FTIR mean calcite mass % and standard deviation (SD) for RCMD samples (excluding Mines 19 and 20) grouped by sampling locations and mining method. As for Figure 5, results were averaged in cases where multiple samples were available in the same mine x location.

Sampling Location	Room and Pillar			Longwall		
	Mean	SD	n	Mean	SD	n
Intake	13.7	6.6	2	36.8	12.4	4
Bolter	10.5	8.1	9	34.3	48.5	2
Feeder	10.3	12.5	9	17.0	0.8	2
Production	1.2	2.4	10	48.7	68.1	2
Return	3.1	3.9	8	52.1	17.0	4

4. Conclusions

Portable FTIR spectroscopy can enable rapid, direct-on-filter (DOF) analysis of respirable coal mine dust (RCMD) samples. While the primary focus of such analysis has been on the measurement of crystalline silica, the potential exists for concurrent measurement of other dust constituents too. These include calcite (calcium carbonate), which is the predominant constituent in many limestone rock dust (RD) products that are applied in coal mines to mitigate explosibility hazards.

Analysis of respirable dust generated from primary dust source materials from 15 underground coal mines across the United States indicated that RD products were the major source of respirable calcite in 13 mines. In such situations, calcite may thus serve as a suitable proxy for the RD contribution to RCMD. However, in the two mines studied here, the roof rock was dominated by limestone, which would confound efforts to use calcite as a proxy for RD in RCMD. As such, a survey of primary dust source materials in any particular mine should be a critical precursor to the interpretation of RCMD results.

With respect to the quality of DOF FTIR measurement of calcite in respirable dust samples, results demonstrated good agreement with other methods (TGA and SEM-EDX)—especially for samples with sufficient total dust mass. Moreover, results were generally consistent with expectations based on the sample source or conditions in the specific mine sampling location. It is noted that no effort was made here to investigate the possible analytical confounders, such as the effects/interferences for calcite in the FTIR spectra due to the mixture of various mineral components in the RCMD samples; though this may be an issue in specific instances and is deserving of attention moving forward. As mentioned earlier, due to the nature of the quantification model, the dust deposition pattern influences the FTIR results. Results suggest that for more accurate quantification, the particle size distribution of calibration samples and samples for analysis should be somewhat similar, which then translates to a similar dust deposition pattern.

Overall, the findings from this study indicate that DOF FTIR can indeed be used to estimate calcite as a proxy for RD in RCMD in many coal mines. Such information may be quite valuable in view of dust source apportionment or tracking spatial and temporal changes in mine conditions.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/min11090922/s1>. Table S1: FTIR, TGA, and SEM-EDX results for respirable dust samples generated from mine dust source materials., Table S2: FTIR, TGA, and SEM-EDX results for RCMD samples.

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