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## A comparison of respirable crystalline silica concentration measurements using a direct-on-filter Fourier transform infrared (FT-IR) transmission method vs. a traditional laboratory X-ray diffraction method

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### ABSTRACT

Evaluation and control of respirable crystalline silica (RCS) exposures are critical components of an effective mine industrial hygiene program. To provide more timely exposure data in the field, an end-of-shift Fourier transform infrared (FT-IR) spectrometry method has been developed for evaluation of direct-on-filter RCS. The present study aimed to apply this FT-IR method using field samples collected in three Northwestern U.S. metal/nonmetal mines and compare the results to traditional laboratory X-ray diffraction analysis (XRD). Seventy-five dust samples were analyzed using both methods. Samples for each mine were split in half by random assignment, with half used to create a calibration factor for the FT-IR analysis and half used to apply the calibration. Nonparametric correlational and two-sample comparative tests were used to assess the strength of association and the level of agreement between the two methods. Strong, positive correlations were observed between FT-IR and XRD RCS concentrations, with Spearman rank correlation coefficients ranging between 0.84 and 0.97. The mean RCS concentrations determined through FT-IR analysis were lower than through XRD analysis, with mean differences ranging from  $-4$  to  $-133$   $\mu\text{g}/\text{m}^3$  and mean percent errors ranging from 12% to 28%. There was a statistically significant improvement in the level of agreement between log FT-IR and log XRD RCS concentrations following calibration at two of the three mines, with mean differences of  $-0.03$  ( $p = 0.002$ ) and  $-0.02$  ( $p = 0.044$ ) in the log scale. The reduction in mean difference following calibration at the other mine was not statistically significant (mean log scale difference =  $-0.05$ ,  $p = 0.215$ ), but the differences between FT-IR and XRD were not significantly different without calibration (mean log scale difference =  $-0.07$ ,  $p = 0.534$ ). The results indicate that mine-specific calibration factors can improve the level of agreement between RCS concentrations determined via a field-based, end-of-shift FT-IR method in metal/non-metal mines as compared to traditional XRD analysis.

### KEYWORDS

Direct-on-filter; Fourier Transform Infrared Transmission (FTIR); respirable crystalline silica (RCS); X-ray diffraction (XRD)

## Introduction

Due to the abundance of silicon dioxide mineral content in the earth's crust, crystalline silica exposure associated with anthropogenic activities is prevalent in many industries, including mining, construction, and manufacturing. There are several polymorphs of crystalline silica, with quartz, cristobalite, and tridymite being those of particular concern. Of these,  $\alpha$ -quartz, a thermodynamically stable form of crystalline silica, is most commonly encountered in industry.<sup>[1]</sup> An analysis of respirable dust samples collected in the United States mining industry

from 1997–2011 revealed a mean percent silica concentration in the metal/nonmetal mining industry and sand and gravel mines of 8.2% and 9.8%, respectively,<sup>[2]</sup> with silica content variability increasing inversely with sample mass. Drilling, cutting, and grinding of source media with even limited crystalline silica concentrations have the potential to disperse substantial amounts of respirable sized particles. The respirable dust dose along with exposure duration and crystalline silica content are all important factors in the development of occupational lung disease.<sup>[3]</sup>

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Silicosis, a form of pulmonary fibrosis, is caused by the inhalation and subsequent deposition of respirable crystalline silica (RCS).<sup>[4]</sup> While the association of RCS exposure and silicosis has been known for over a century, the U.S. Occupational Safety and Health Administration (OSHA) estimates that 2.3 million U.S. workers remain at risk.<sup>[5]</sup> A recent review of silicosis deaths in the U.S. revealed a statistically significant decline from 164 (death rate = 0.74 per 1 million population) in 2001 to 101 (0.39 per 1 million) in 2010 ( $p = 0.002$ ). While these statistics appear promising, new occupations and tasks (hydraulic fracturing of gas and oil wells and fabrication and installation of engineered stone countertops) were identified in addition to traditional occupations that place workers at risk for silicosis.<sup>[6]</sup> Of the mining industry silicosis deaths from 1990–1999, 86 (42%) occurred in metal mining.<sup>[7]</sup> In addition to silicosis, RCS exposure increases the risk of emphysema, bronchitis, tuberculosis, and renal disease.<sup>[8,9]</sup> Crystalline silica dust (quartz and cristobalite) is classified as a Class I human carcinogen by the International Agency for Research on Cancer.<sup>[10]</sup>

Historically, in the United States regulatory occupational exposure limits for respirable dust containing silica have been dynamic values with reductions based on the quantity of crystalline silica in the sample.<sup>[11–14]</sup> These exposure limits consider the three polymorphs of crystalline silica (quartz, cristobalite, and tridymite). Both OSHA (historically) and MSHA (metal/nonmetal sector only, e.g., mining operations other than coal) define a further reduction (1/2 that calculated for quartz) in the allowable exposure limit for respirable samples containing cristobalite and/or tridymite.<sup>[11,14]</sup> The American Conference of Governmental Industrial Hygienists (ACGIH<sup>®</sup>) recommends a threshold limit value (TLV) for RCS (quartz and cristobalite) of 0.025 milligrams per cubic meter ( $\text{mg}/\text{m}^3$ ).<sup>[15]</sup> Recent regulatory efforts in the U.S. have resulted in an OSHA final revised 8-hr time-weighted average (TWA) RCS (quartz and cristobalite) standard with a single-value permissible exposure limit of 50 micrograms per cubic meter ( $\mu\text{g}/\text{m}^3$ ), coupled with an action level of 25  $\mu\text{g}/\text{m}^3$ . This final rule on silica became effective June 23, 2016, with initially 1 and 2 years allotted for construction and general industry/maritime compliance, respectively.<sup>[5]</sup> OSHA extended this enforcement date in the construction industry to September 23, 2017, citing the need for additional outreach and enforcement personnel training.<sup>[16]</sup> MSHA indicated in its regulatory agenda that it will consider a similar revision to the

rule for crystalline silica exposure limits for metal/nonmetal mines, but for now the strategy for a respirable dust exposure limit remains a dynamic value based on the quantity of crystalline silica.

Silicosis is a preventable disease. Regular evaluation of worker breathing zone RCS exposures along with applicable control measures are critical components to an effective disease prevention strategy. Current air sampling techniques for RCS include the use of a cyclone for the size separation and collection of respirable particles (4- $\mu\text{m}$  50% cut-point) on polyvinyl chloride (PVC) filter media.<sup>[17]</sup> The gravimetric respirable dust concentration, along with the crystalline silica concentration, is then typically quantified by an independent laboratory. The two principal analytical techniques used to quantify RCS are X-ray diffraction (XRD) and mid-infrared spectrometry (IR). Of these, XRD is specified for metal/nonmetal mining (NMAM 7500)<sup>[18]</sup> and OSHA (ID-142)<sup>[19]</sup> compliance, while IR is used for coal dust RCS analyses.<sup>[20,21]</sup> While direct-on-filter RCS analysis employing IR and XRD is specified in some international methods,<sup>[22]</sup> in the U.S., IR and XRD laboratory analyses are currently indirect methods which require multiple laboratory preparation steps to analyze the RCS concentration. These steps include pre- and post-filter weighing, muffle furnace, plasma ashing, or solvent dissolution to remove the filter and organic interferences, and redeposition of the sample onto a separate filter or into a potassium bromide pellet, followed by analysis. These preparation steps are time consuming, and, as a result, RCS laboratory results are typically not available for 1–2 weeks, potentially delaying industrial hygiene control strategies and worker protection. This slow turnaround of data is especially impactful in occupational environments with rapidly changing exposure conditions.

Field-based analytical techniques for RCS are currently not available commercially. The Pittsburgh Mining Research Division, a division of the National Institute for Occupational Safety and Health (NIOSH), initiated a program to evaluate the application of a field-portable, end-of-shift, direct-on-filter method for RCS measurement. Direct-on-filter quantification of RCS via IR works without ashing and sample redeposition laboratory preparation and has been demonstrated as a viable method for quantifying RCS.<sup>[23,24]</sup> This technology will potentially enable an on-site industrial hygienist to quantify RCS at the conclusion of the sampling period. While XRD is advantageous in that it can distinguish between the polymorphs of crystalline silica, IR technology was

selected due to its widespread availability, cost, field portability, and ease of use. Recognized disadvantages of IR technology include limitations resulting from absorption peak interferences.<sup>[22,25]</sup> When infrared absorption spectra are graphed, the absorbance peak of crystalline silica is at or near a wave number of  $800\text{ cm}^{-1}$ . Additional minerals in the sample, such as clay- and mica-based minerals that have absorption peaks coinciding with this crystalline silica analytical peak, may produce erroneous results, and spectrum corrections for these confounding minerals typically must be applied.<sup>[21,25]</sup>

Several applications of IR technology exist. Fourier transform IR (FT-IR) spectrometry has been most commonly used in field-portable, end-of-shift, direct-on-filter assessments.<sup>[26–31]</sup> FT-IR uses an IR emitting source to illuminate the sample with numerous wavelengths over a wide spectral range. The raw data from the returning signal must then be analyzed mathematically by a Fourier transform algorithm.<sup>[32]</sup> FT-IR may be operated in several different modes including transmission, diffuse reflection, and attenuated total reflection. FT-IR performed in the transmission mode has been demonstrated as an effective method for quantifying  $\alpha$ -quartz directly on PVC filter media obtained from laboratory-generated coal dust<sup>[26,27,29]</sup> as well as PVC filter media from active coal mines.<sup>[31]</sup> The FT-IR technique yielded strong correlations with the IR MSHA P7 integrated laboratory method when a correction for kaolin clay, a major confounding mineral associated with coal dust, was applied.<sup>[26]</sup> The correlation of silica mass detected with FT-IR vs. the IR MSHA P7 method was strengthened with a partial least squares regression of the transmission spectra approach.<sup>[31]</sup> Weakely et al. expanded this research into non-coal mines with analysis of respirable dust from field surveys collected from silver, granite, and limestone mines, and demonstrated that partial least squares regression of the transmission spectra most accurately predicted silica mass relative to laboratory XRD analysis.<sup>[28]</sup> To date, no comparisons between metal/nonmetal RCS concentrations analyzed using FT-IR and XRD have been reported in the scientific literature. Such a comparison is needed before the FT-IR method can be employed by industrial hygienists to evaluate occupational RCS exposures in the metal/nonmetal mining industry.

The goal of this study was to demonstrate the application of RCS concentration analysis via FT-IR in comparison with results obtained via laboratory XRD analyses using field samples collected from three metal/nonmetal mines. The goal will be addressed

through three research objectives. First, the strength of the associations between RCS concentrations at each mine using the FT-IR and XRD methods will be assessed. Second, a prediction equation will be developed to predict XRD concentrations given FT-IR concentrations for each mine. Finally, the level of agreement between the FT-IR RCS concentrations, the predicted XRD concentrations, and the actual XRD concentrations will be evaluated.

## Methods and materials

Area air sampling for RCS was conducted in three metal/nonmetal mines in the northwestern United States, including an underground gold mine (Mine A), a surface copper mine (Mine B), and an underground silver/lead/zinc mine (Mine C).

In Mines A and B, which were actively producing mines, the area sampling was conducted in the same locations (near crushing and conveying processes) during each sample day. These areas were selected with assistance from mine management and were designated as the areas and processes in the facilities that were anticipated to generate the highest concentrations of particulate matter. Mine C was a non-producing, university campus mine training lab housed in an historic underground silver/lead/zinc mine abandoned in the mid-1950s. No crushing and conveying processes occur at Mine C, unlike at Mine A and Mine B. Mine C is used to train students in underground mining practices and does not produce a saleable product. Student mining occurs in the host rock and activities are for instructional purposes. Since ore was not processed from this facility, area sampling was instead performed near tasks anticipated as most likely to generate the largest fraction of particulate matter. Dust-generating tasks included jackleg drilling, blasting, and mucking.

Respirable dust area air sampling was performed at each mine site using GK 2.69 cyclones paired with 37-mm three-piece cassettes, low ash polyvinyl chloride (PVC) filters with a pore size of  $5\ \mu\text{m}$ , and SKC Airchek pumps. The GK 2.69 cyclones were pre- and post-calibrated using a high-flow Bios Defender Drycal primary flow meter at  $4.2\ \text{L}/\text{min}$ . Sample durations ranged from 2–5 hr, and sample volumes were within the recommended limits according to the NIOSH methods for silica determination—NIOSH7500, NIOSH7602, and NIOSH7603.<sup>[18,20,33]</sup>

Gravimetric analysis of dust samples was performed via the NIOSH Manual of Analytical Methods (NMAM) 0600, particles not otherwise regulated,

respirable.<sup>[17]</sup> Samples were then analyzed by FT-IR with a Bruker Optics model Alpha FT-IR spectrometer operated in the transmission mode at  $4\text{ cm}^{-1}$  resolution to determine the RCS concentration in  $\mu\text{g}/\text{m}^3$ . Because the samples are unaltered during the FT-IR analysis, it was possible to perform subsequent analysis on the same samples. All the samples were submitted for further analyses via XRD by an independent American Industrial Hygiene Association (AIHA<sup>®</sup>) accredited lab via NIOSH 7500, crystalline silica by XRD (filter redeposition).<sup>[18]</sup>

The limit of quantification (LOQ) for respirable dust analysis was  $5\ \mu\text{g}$ . The limit of detection (LOD) and LOQ for RCS analysis via the FT-IR method were 5 and  $15\ \mu\text{g}$ , respectively, while the LOQ for RCS via XRD through the accredited lab was  $17\ \mu\text{g}$ . Only samples meeting or exceeding the RCS LOQ values were considered for data analysis.

In addition to the respirable dust air sampling, a minimum of three bulk ore samples were collected at each mine to characterize the mineral content of the ore. 500 g of bulk ore fine particulate were collected within close proximity of the air sampling sites and placed in labeled, sealed, plastic bags. The bulk samples were later analyzed via XRD with the Rietveld quantification method.<sup>[34]</sup>

### Statistical analysis

To assess the first research objective, a Spearman rank-order correlational analysis was performed between the FT-IR and XRD RCS concentrations at each mine. Spearman correlation was used because the RCS concentration data were not normally distributed for the mines assessed during this study. Log transformation was explored to employ Pearson correlation, but the data were still not normally distributed following the transformation.

To address the second research objective, each RCS concentration was log-transformed and each pair of concentration measurements (including one FT-IR result and a matching XRD result) was assigned a random number. Half of the pairs from each mine were selected using the lowest half of the random numbers. This selected half of the measures was used to model the relationship between FT-IR and XRD RCS concentrations at each mine and to create a prediction equation for finding an XRD RCS concentration given a FT-IR concentration using a linear regression model. Inverse regression (or calibration) was used for the prediction equation, because we were predicting the standard value (XRD RCS concentration) given a

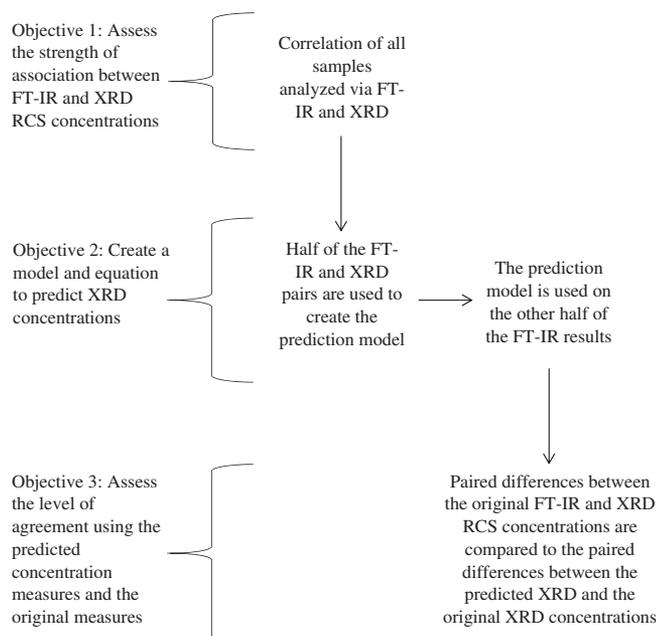
value obtained with the new method (FT-IR RCS concentration). The prediction equation was used on the unselected, log-transformed FT-IR RCS concentrations to determine the expected log-transformed XRD value based on the model generated for each mine. Log transformation was utilized to improve the normality and homoscedasticity of the errors, as assessed via qualitative assessment of diagnostic residual plots for each regression. Residuals were computed as the difference between the observed FT-IR concentration minus the modeled FT-IR concentration for each data point.

Finally, to assess the third research objective, a Wilcoxon rank sum test was used to compare the original, unselected FT-IR and XRD concentration differences to the predicted XRD and original XRD concentration differences for each mine. The null hypothesis for each mine was that there would be no significant improvement in the level of agreement (as indicated by a decrease in mean difference) using the prediction equation. The level of agreement analysis was also completed in the log-scale, because the linear models used to generate the prediction equation used log-transformed variables. A nonparametric analysis was used to assess the level of agreement despite the use of log-transformed variables because the log-scale differences were not normally distributed for all mines. Level of agreement between the two methods is a measure of accuracy of the FT-IR analysis as compared to the benchmark XRD analysis. To provide another measure of agreement using the original scale (untransformed) variables, a qualitative Bland-Altman plot analysis was also conducted on the raw RCS concentrations as determined using FT-IR and XRD analyses for each mine.

A flowchart is provided in [Figure 1](#) that details the experiment. The level of statistical significance for all analyses was set at  $\alpha=0.05$ . All statistical analyses were performed using Minitab 17 Statistical Software (Version 17.1.0, State College, PA).

### Results

Summary data for the air sampling conducted in the three mines are provided in [Table 1](#). Of the 40 samples collected from Mine A over 9 days, 10 samples did not meet the  $15\ \mu\text{g}$  LOQ criteria. Twenty-five of the 27 samples collected during 9 sampling days from Mine B met the LOQ criteria. Of the 29 samples collected over 11 days from Mine C, 18 samples did not meet the  $15\text{-}\mu\text{g}$  sample silica criteria. It is postulated that the limited activities in Mine C, limited sample



**Figure 1.** Experimental design flowchart for each mine.

**Table 1.** Respirable crystalline silica samples collected at three Northwestern U.S. mines.

	Mine A	Mine B	Mine C
Number of samples initially collected	40	27	29
Number of samples meeting LOQ	30	25	20 <sup>a</sup>

<sup>a</sup>Nine respirable dust samples were obtained using bulk material from Mine C via chamber dispersion.

LOQ = Limit of quantification

durations, and effective dust control measures were factors. In order to ensure an adequate number of samples, bulk material from Mine C was dispersed via air flowing into a glass vessel containing the dust, which fed aerosolized material into a calm air dust chamber, and nine additional respirable dust samples were collected employing the same sampling methods previously described. All of these additional samples met the silica LOQ requirements and were included in the XRD and FT-IR analysis for Mine C, for a total of 20 viable samples, as reported in Table 1.

The mean percent silica for samples meeting the LOQ criteria as determined via FT-IR in each mine was 20.3% for Mine A, 13.4% for Mine B, and 13.5% for Mine C. The geometric mean RCS concentration obtained via FT-IR and XRD were 96 and 105  $\mu\text{g}/\text{m}^3$ , respectively, for Mine A, 125 and 161  $\mu\text{g}/\text{m}^3$  for Mine B, and 300 and 398  $\mu\text{g}/\text{m}^3$  for Mine C. The mean percent error between the RCS concentrations as determined using FT-IR relative to the concentrations determined via XRD was 12%, 22%, and 28% at Mine A, B, and C, respectively. The RCS concentrations statistics for each mine analyzed using both

methods are presented in Table 2. A strong, positive association was observed between FT-IR and XRD RCS concentrations. The Spearman correlation coefficient for the FT-IR and XRD RCS concentrations was 0.97 for Mine A, 0.86 for Mine B, and 0.96 for Mine C. Spearman coefficients for each mine are shown in Figure 2.

The RCS concentrations measured at each mine were log-transformed, and the matched FT-IR and XRD pairs were assigned random numbers. Half of the pairs were randomly selected to construct linear regression models for each mine. The linear model proved to be a good fit for the data, with R-squared values of 98.7%, 96.8%, and 87.8% for Mines A, B, and C, respectively. The regression coefficients for Mines A, B, and C were 1.07, 1.15, and 0.99, respectively. Fitted-line plots and regression model equations for each mine are shown in Figure 3.

The mean differences between the original log-transformed FT-IR RCS concentrations and the original log-transformed XRD concentrations for the unselected half of the data were  $-0.072$  for Mine A,  $-0.120$  for Mine B, and  $-0.134$  for Mine C. The mean differences between the predicted log-transformed XRD concentrations and the original log-transformed XRD concentrations at each mine were  $-0.049$ ,  $-0.027$ , and  $-0.021$ , respectively. There was a statistically significant reduction in the mean differences in log concentrations for Mine B ( $p = 0.002$ ) and Mine C ( $p = 0.044$ ) when using the predicted XRD concentrations as compared to the original FT-IR data. The improved level of agreement

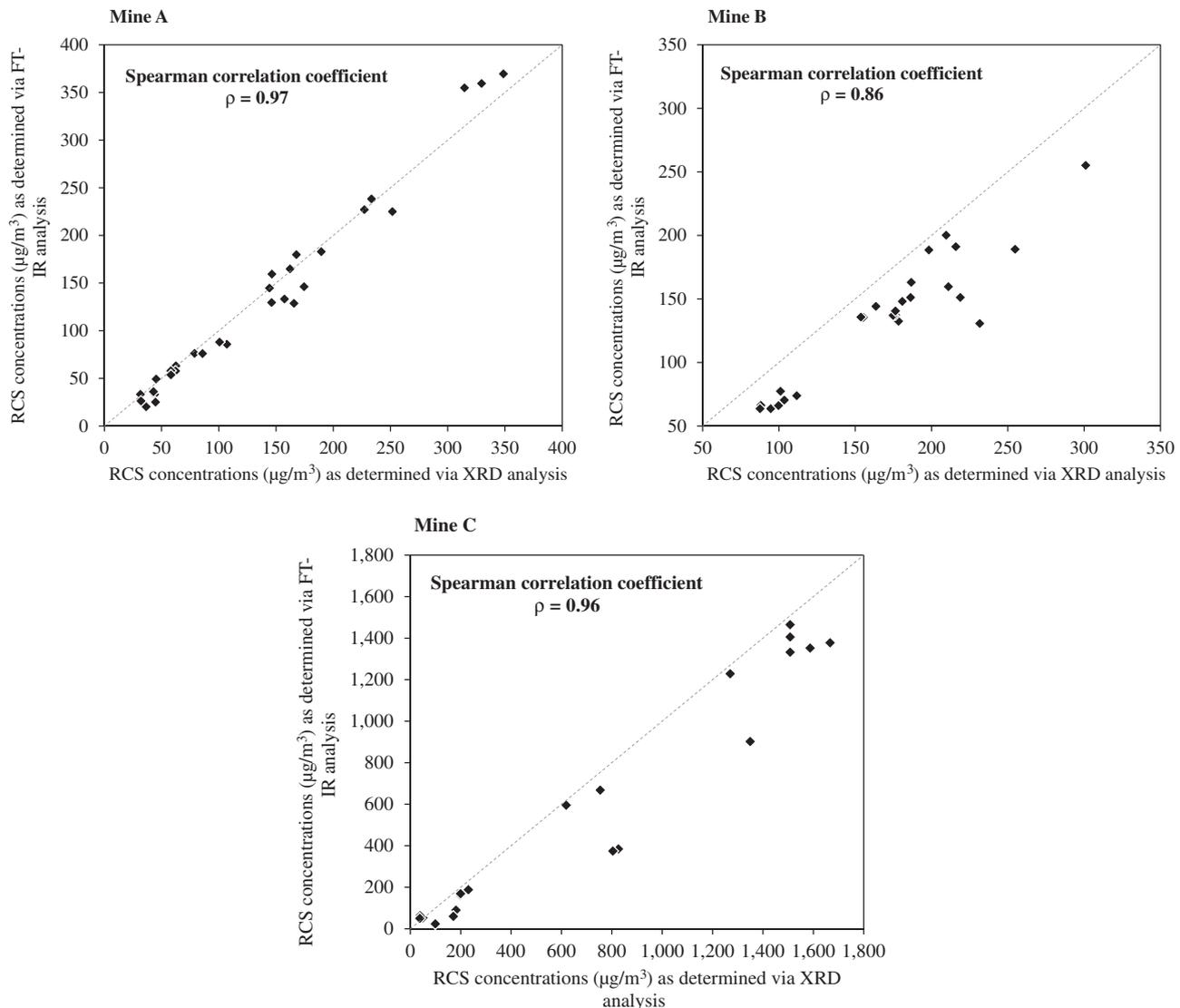
**Table 2.** Respirable crystalline silica concentration as determined via FT-IR and XRD analysis for Mines A, B, and C.

	Mine A $n = 30$ ( $\mu\text{g}/\text{m}^3$ )		Mine B $n = 25$ ( $\mu\text{g}/\text{m}^3$ )		Mine C $n = 20$ ( $\mu\text{g}/\text{m}^3$ )	
	FT-IR	XRD	FT-IR	XRD	FT-IR	XRD
Arithmetic mean (SD)	131 (101)	135 (93)	135 (50)	170 (56)	597 (563)	730 (623)
Geometric mean (GSD)	96 (2)	105 (2)	125 (2)	161 (1)	300 (4)	398 (4)
Standard error	19	17	9	10	103	114
Coefficient of variation (unitless)	0.77	0.69	0.37	0.33	0.94	0.85
Mean % error (SD)	12% (11%)		22% (10%)		28% (24%)	
Bias (mean FT-IR – mean XRD)	–4		–36		–133	

FT-IR = Fourier transform infrared spectrometry

XRD = X-ray diffraction

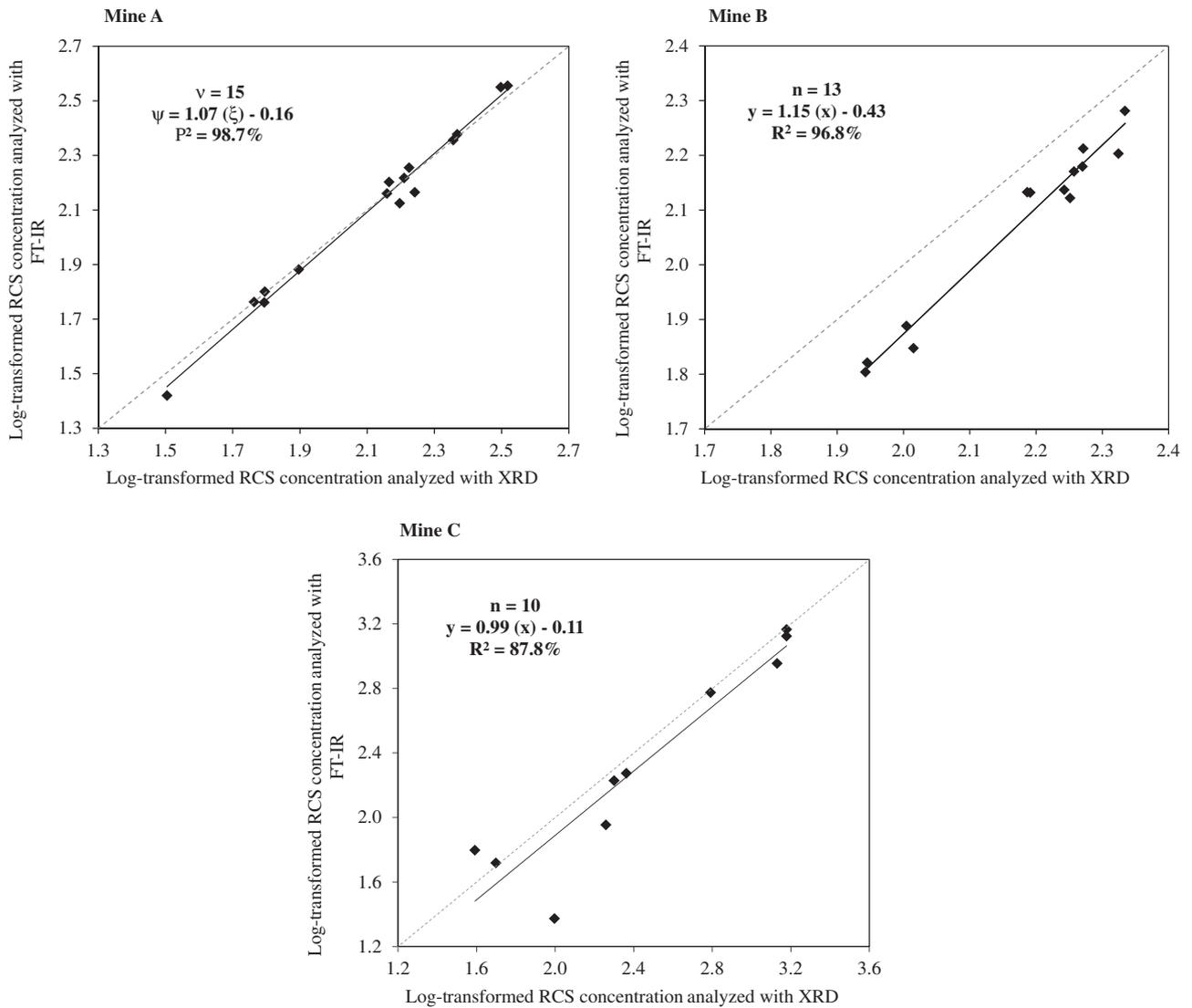
SD = Standard deviation

**Figure 2.** A comparison of RCS concentrations obtained from Mine A, Mine B, and Mine C by FT-IR and traditional XRD analyses.

for Mine A was not statistically significant ( $p = 0.215$ ). The quantitative levels of agreement analysis results are summarized in Table 3.

A follow-up analysis was performed to determine if the lack of a statistically significant improvement in the level of agreement for Mine A following

correction was due in part to the high level of agreement in the original data. A Wilcoxon rank sum test was performed to see if there was a difference between the mean log-transformed FT-IR RCS concentrations and the mean XRD RCS concentrations at Mine A without applying a correction factor. Indeed, there



**Figure 3.** Relationship between log-transformed RCS concentrations as determined via FT-IR and XRD analysis for Mine A, Mine B, and Mine C for mine-specific FT-IR calibration. The solid line indicates regression equation, the dashed line illustrates 1:1 agreement.

**Table 3.** Level of agreement analysis for log-transformed respirable crystalline silica concentrations from FT-IR and XRD methods, as well as predicted log-transformed XRD concentrations for Mines A, B, and C.

	Mine A n = 15	Mine B n = 12	Mine C n = 10
Original comparison	Log FT-IR - Log XRD	Log FT-IR - Log XRD	Log FT-IR - Log XRD
Mean difference (SD)	-0.07 (0.09)	-0.12 (0.07)	-0.13 (0.16)
Prediction comparison	Predicted Log XRD - Log XRD	Predicted Log XRD - Log XRD	Predicted Log XRD - Log XRD
Mean difference (SD)	-0.05 (0.08)	-0.03 <sup>a</sup> (0.06)	-0.02 <sup>a</sup> (0.17)

<sup>a</sup>Improvement in the level of agreement was statistically significant at the  $\alpha = 0.05$  level

FT-IR = Fourier transform infrared spectrometry

XRD = X-ray diffraction

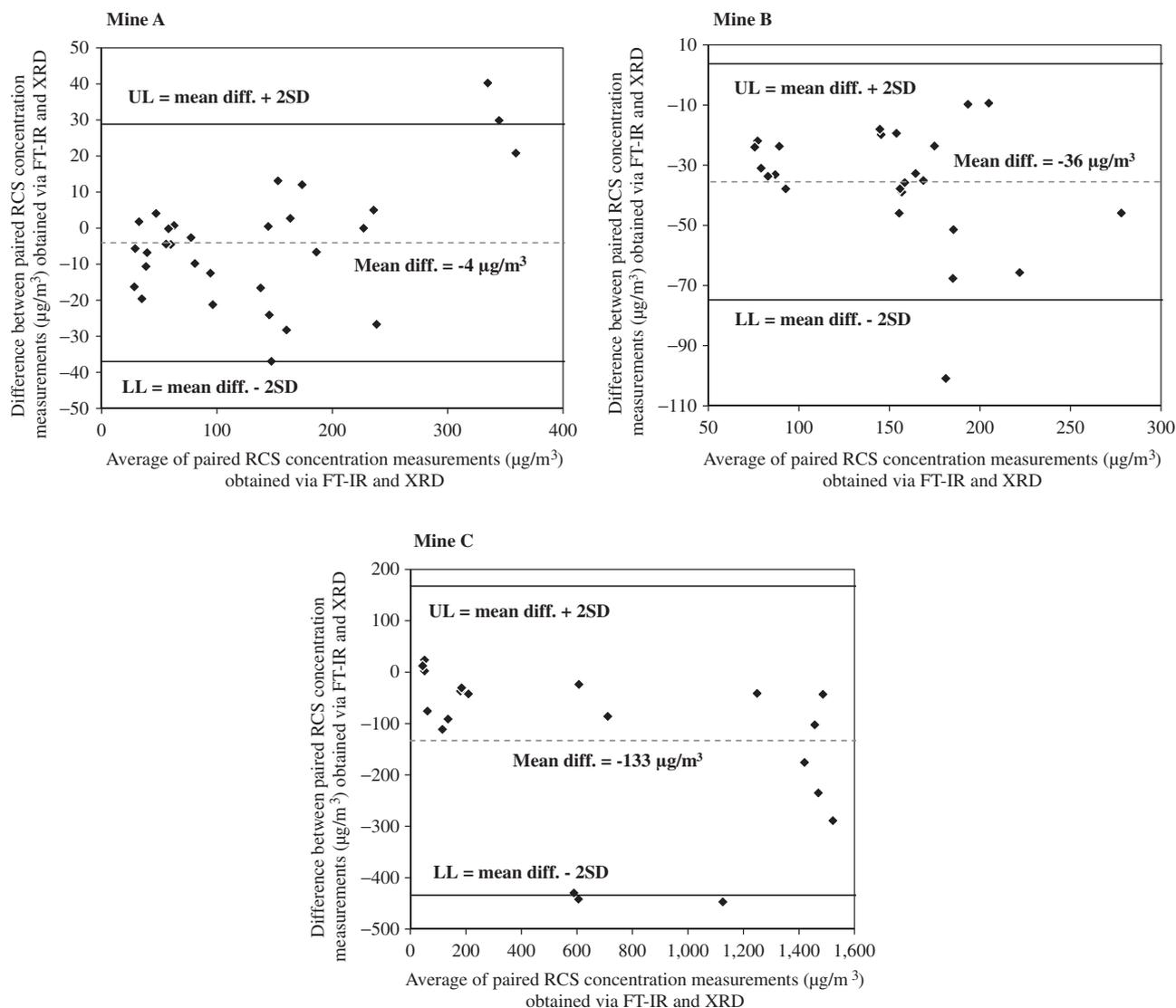
SD = Standard deviation

was no statistically significant difference between the two analytical methods without the use of a calibration correction ( $p = 0.534$ ).

The qualitative Bland-Altman plots using untransformed data for each mine are provided in Figure 4. The method mean differences (bias) and 95% limits of

agreement are provided in the plots. Generally, most of the paired difference fell within the limits of agreement, and the variability of agreement increased as the average of the paired measurements increased.

In addition to quartz, other minerals were identified in the bulk samples collected from each mine.



**Figure 4.** Bland-Altman plots comparing paired RCS concentration differences (FT-IR – XRD) to concentration averages from Mine A, Mine B, and Mine C. The solid lines indicate limits of agreement (UL is the upper limit, LL is the lower limit) and the dashed line indicates the mean difference between analytical methods.

Quartz, albite, and muscovite were common in all three mines. In addition to these minerals, Mine A contained orthoclase, pyrite, and jarosite; Mine B contained calcite, microcline, kaolinite, and montmorillonite; and Mine C contained calcite, kaolinite, montmorillonite, orthoclase, basanite, bloedite, hornblende, and apatite. The mean percentage by weight of crystalline silica (quartz) present in the bulk samples was 22.7% for Mine A, 25.7% for Mine B, and 16% for Mine C.

## Discussion

The variability of the RCS concentrations as determined using the two methods were fairly comparable, as evidenced by similar standard errors and standard

deviations (Table 2). The observed level of precision of FT-IR in this study was consistently lower than XRD with higher coefficients of variation observed at each mine, although FT-IR was within 10% of XRD coefficient in each case.

Three research objectives were proposed to demonstrate the application of RCS concentration analysis via FT-IR in comparison with results obtained via laboratory XRD analyses using field samples collected from three metal/nonmetal mines. The initial objective was to assess the strength of association between RCS concentrations at each mine using FT-IR and XRD methods. The results of this study demonstrate that direct-on-filter analysis of RCS concentrations analyzed via FT-IR were highly correlated with results obtained via laboratory XRD analysis. Strong, positive

correlations between FT-IR and XRD RCS concentrations in this study ranging from 0.86–0.97 are comparable to those reported by Miller et al.<sup>[26]</sup> (0.90–0.97)<sup>[26]</sup> in an assessment of crystalline silica mass in coal dust via FT-IR vs. the MSHA P7 analytical method.

In the second objective of this study, we demonstrated that an inverse linear regression model can be used to predict log-transformed XRD RCS concentrations given FT-IR RCS concentrations and to generate a site-specific calibration correction factor. The simple linear model proved to be a good fit for the data. The high  $R^2$  values confirm that virtually all of the variability observed in FT-IR-derived RCS concentrations can be explained by the variability observed in the XRD concentrations. Further, the regression coefficients (slopes) observed in each mine's linear model using RCS concentration in the log-scale were close to 1 (range 0.99–1.15, as shown in Figure 3).

The mine-specific calibration factor derived from the inverse linear regression model was applied to the second half of the paired data set for each mine. Considering this calibration factor, the level of agreement between the FT-IR RCS concentrations, the predicted XRD concentrations, and the actual XRD concentrations was then evaluated to fulfill objective three. Of the three mines, prior to any statistical modeling, the strongest positive association between FT-IR and XRD RCS concentrations was observed with Mine A. When the calibration factor was applied to the second half of paired data for Mine A, an improved level of agreement was observed but the improvement was not statistically significant. As verified by the follow-up analysis, this insignificant improvement was likely attributable to the already very high level of agreement between both methods at Mine A. The correction factor did result in a statistically improved level of agreement for Mines B and C. These results suggest that while strong, positive correlations were initially observed in RCS data obtained via FT-IR and XRD analysis, the application of a correction factor, specific to each mine, improves the prediction of XRD RCS concentrations using FT-IR.

The qualitative Bland-Altman plot analysis revealed important information related to the untransformed results from each mine. First, the bias for each mine was negative, indicating that the FT-IR tended to underestimate RCS concentrations as compared to XRD. Second, the limits of agreement, like the data themselves, varied considerably for each mine, from a relatively narrow range of differences of approximately 70  $\mu\text{g}/\text{m}^3$  for Mines A and B, to a range of over

500  $\mu\text{g}/\text{m}^3$  for Mine C. As no target limits of agreement were established for this study a priori, it is inappropriate to comment on the adequacy of the ranges. However, for comparison, the Bland-Altman limits of agreement for two inhalable dust samplers was 480  $\mu\text{g}/\text{m}^3$  (upper limit: a mean difference of 0.27  $\text{mg}/\text{m}^3$ , lower limit: a mean difference of  $-0.21 \text{ mg}/\text{m}^3$ ).<sup>[35]</sup> In addition, the increasing variability of the differences observed in this study as the average between the paired measurements increased suggest that the use of log-transformation of RCS concentration differences is indicated.

Development of a correction factor specific to each mine through an inverse linear regression approach indirectly addresses the presence of mineral interferences in a specific dust assuming that their content is relatively consistent. While analysis of mineral interferences was not the primary scope of this research, additional minerals, identified through analysis of bulk mineral samples collected from each mine, were present. In addition to kaolinite, minerals characterized through IR absorption bands that may coincide or overlap with the crystalline silica absorption band (800  $\text{cm}^{-1}$ ) include muscovite (799  $\text{cm}^{-1}$ ), montmorillonite (797  $\text{cm}^{-1}$ ), and albite and orthoclase (788  $\text{cm}^{-1}$ ).<sup>[23]</sup> Several of these minerals were observed in bulk sample analysis, with the highest fraction in Mines B and C. Because the calibration significantly improved the level of agreement in these mines, this finding may suggest that higher fractions of mineral interferences in the respirable dust sample increase the need for and effect of a site-specific correction factor.

### Study limitations

A limited number of metal/nonmetal mines and respirable dust samples were considered for this research. Several logistical challenges limited the amount of sampling that could be conducted at each mine during this study. Future evaluations should look at collecting a larger set of samples for site-specific calibration and then conducting follow-up sampling using the correction factor under different sampling circumstances.

All of the respirable dust samples were collected via area sampling techniques as compared to worker personal breathing zone samples. In addition, as the FT-IR end-of-shift direct-on-filter technology continues to develop, the methodology should be applied to the analysis of typical personal breathing zone samples as compared to the high dust area samples that were the focus of this study.

To overcome the issue related to the collection of respirable dust material sufficient for direct-on-filter analysis with the portable FTIR, an independent study was published reporting the development of a novel respirable dust sampler. This dust sampler employs a 25 mm diameter filter, which concentrates the dust sample in a smaller area on the filter media relative to 37-mm filters,<sup>[36]</sup> therefore, inducing a higher sensitivity for the silica analysis conducted with the direct-on-filter technology. It also features a filter cassette that can be removed from the sampler and placed directly in the portable FTIR instrument, with no need to remove the filter from the cassette.

The development of the correction factor specific to each mine addressed the presence of other minerals for the three mines. In other cases, the authors recognize that a more mineral-specific correction factor might be needed. For example, a multivariate partial least squares regression analysis of the transmission spectra strengthened the correlation of silica mass detected on coal dust samples analyzed with FT-IR vs. the IR MSHA P7 method.<sup>[31]</sup> This analytical technique has also resulted in accurate prediction of silica mass via FT-IR relative to laboratory XRD analysis in respirable dust samples collected in metal/nonmetal mines for samples with minimal interferences.<sup>[28]</sup> Partial least squares regression is advantageous in that a correction for kaolin or other mineral interferences is not required; however, it requires a full IR spectral analysis to develop a calibration value relative to a standard laboratory method.

Nine samples from Mine C were collected via a chamber dispersion method due to the challenge of achieving the 15- $\mu\text{g}$  silica mass LOQ with field sampling. These samples may therefore not have been representative of the particle size distribution and silica concentrations typically encountered in that mine. This may be one reason why the observed associations and level of agreement at Mine C were lower than at the other two mines. However, we did use bulk material collected from the same location to generate aerosols in the chamber for the nine additional samples, and the observed associations were still rather strong.

Optimum samples meeting or exceeding the RCS mass LOQs were considered in this study. Samples below the direct-on-filter FT-IR LOQ of 15  $\mu\text{g}$  and/or the laboratory XRD LOQ of 17  $\mu\text{g}$  were not included in the statistical analysis. The approach was used to ensure a high level of confidence in the data used for a comparison of the two methods; however, this resulted in only 66 of 96 samples (69%) in the original

data set meeting the LOQ required for valid field samples. The desirable decrease in the RCS amount in respirable dust samples connected to mining environments, potentially associated with the promulgation by MSHA of a lower PEL for RCS, could create an issue related to the direct-on-filter FT-IR LOQ of 15  $\mu\text{g}$ . The use of high-flow rate samplers, like those used in this study, can be a valuable solution for this issue.

The FT-IR analysis was performed at the NIOSH Pittsburgh Mining Research Division Lab by research laboratory technicians with expertise in IR techniques. The field application of FT-IR should be expanded with future end-of-shift FT-IR measurements conducted by occupational safety and health personnel with limited research expertise in FT-IR techniques. In this case, the authors recognize the need for and benefit of specific manuals, standard operating procedures, and even a specialized software interface to guide inexperienced users to conduct this analysis independently.

## Conclusions

The application of FT-IR technology to field samples collected in three Northwestern U.S. metal/nonmetal mines was assessed in comparison with results obtained through traditional XRD analysis. The FT-IR method resulted in mean RCS concentrations that were lower than the XRD method. The variability of the two methods was similar, and the observed level of precision was somewhat lower for the FT-IR method. Strong, positive correlations were observed between FT-IR and XRD RCS concentrations for each mine. The application of a mine site-specific calibration factor obtained through inverse linear regression significantly improved the level of agreement between the two analytical methods in two out of the three mines. A high level of agreement between both methods without any correction was noted in the mine that was not significantly improved by the correction factor. These results suggest that the FT-IR method is capable of delivering more timely RCS exposure concentrations that are comparable with those obtained through the slower, traditional XRD laboratory method.

This article demonstrates a simplified approach for adjusting FT-IR data to reduce the difference with standard XRD analysis via a mine specific correction factor. The application of this end-of-shift technology, if implemented by non-FT-IR experts such as industrial hygienists, could substantially decrease analytical

delays associated with current integrated crystalline silica analyses, and thus improve the application of appropriate industrial hygiene control strategies and worker protection measures. This end-of-shift feedback of sampling results is especially impactful in mining environments where geological conditions and subsequent RCS exposures may change rapidly, however, the approach is also applicable to non-mining environments.

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