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Evaluation of Diffuse Reflection Infrared Spectrometry for End-of-Shift Measurement of α -quartz in Coal Dust Samples

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Abstract

The inhalation of toxic substances is a major threat to the health of miners, and dust containing respirable crystalline silica (α -quartz) is of particular concern, due to the recent rise in cases of coal workers' pneumoconiosis and silicosis in some U.S. mining regions. Currently, there is no field-portable instrument that can measure airborne α -quartz and give miners timely feedback on their exposure. The U.S. National Institute for Occupational Safety and Health (NIOSH) is therefore conducting studies to investigate technologies capable of end-of-shift or real-time measurement of airborne quartz. The present study focuses on the potential application of Fourier transform infrared (FT-IR) spectrometry conducted in the diffuse reflection (DR) mode as a technique for measuring α -quartz in respirable mine dust. A DR accessory was used to analyze lab-generated respirable samples of Min-U-Sil 5 (which contains more than 90% α -quartz) and coal dust, at mass loadings in the ranges of 100–600 μg and 600–5300 μg , respectively. The dust samples were deposited onto three different types of filters, borosilicate fiberglass, nylon, and polyvinyl chloride (PVC). The reflectance, R , was calculated by the ratio of a blank filter and a filter with deposited mine dust. Results suggest that for coal and pure quartz dusts deposited on 37 mm PVC filters, measurements of $-\log R$ correlate linearly with known amounts of quartz on filters, with R^2 values of approximately 0.99 and 0.94, respectively, for samples loaded up to ~ 4000 μg . Additional tests were conducted to measure quartz in coal dusts deposited onto the borosilicate fiberglass and nylon filter media used in the NIOSH-developed Personal Dust Monitor (PDM). The nylon filter was shown to be amenable to DR analysis, but quantification of quartz is more accurate when the filter is "free," as opposed to being mounted in the PDM filter

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holder. The borosilicate fiberglass filters were shown to produce excessive interference, making quartz quantification impossible. It was concluded that, while the DR/FT-IR method is potentially useful for on-filter measurement of quartz in dust samples, the use of PVC filters produced the most accurate results.

Keywords

coal dust; diffuse reflection spectrometry; silica; α -quartz

INTRODUCTION

Inhalation of dust containing respirable crystalline silica (RCS) can cause silicosis, which reduces the lung's capability to extract oxygen from the air.⁽¹⁾ Studies by the U.S. National Institute for Occupational Safety and Health (NIOSH) have been important in documenting the extent of silicosis in occupational settings,⁽²⁾ including data showing that a quarter of the deaths occurred in the mining industry, and that only about one in six death certificates of people who died of silicosis identified it as a cause of death.⁽³⁾ Presently, more than 1 million U.S. workers are routinely exposed to RCS, and each year more than 250 American workers die from silicosis.⁽²⁾

Despite extensive knowledge regarding exposure hazards and effective mitigation measures, exposure to RCS continues, and is particularly high in the mining industry, for both coal and non-coal miners.^(2,4,5) Exposure to silica-bearing coal dust can lead to silicosis and coal workers' pneumoconiosis (CWP). Recently there has been an increase in the number of cases of CWP in the United States⁽⁶⁾ and lung disease among miners continues to be a problem.⁽⁷⁾ This highlights the importance of reducing miners' exposure to coal dust as well as the RCS (particularly α -quartz) that it may contain.

To help monitor exposure to dust in mining environments, NIOSH developed a direct reading personal dust monitor (PDM) for measuring miners' exposure to respirable coal mine dust (RCMD).⁽⁸⁻¹⁰⁾ The PDM is a belt-worn module that allows miners to obtain real-time information on their levels of dust exposure. It has successfully aided miners in reducing their exposure to RCMD by allowing them to make changes in their work activities based on the continuous output of the device,⁽¹¹⁾ but does not provide information specific to silica exposure. Coal miners' exposure to silica is determined by collecting a filter sample and analyzing it using a lab-based procedure that uses Fourier transform infrared (FT-IR) spectrometry, known as the P7 analytical method.^(12,13) Since the lab-based process can take weeks before exposure data are received, the information is not always helpful in improving workplace conditions. NIOSH is conducting research to evaluate the potential impact of the PDM toward reducing miners' exposure to RCMD.⁽¹⁰⁾ Current studies are aimed at reducing exposure to respirable quartz, including evaluation of spectrometric methods amenable to end-of-shift (EOS) measurement of silica in samples of RCMD collected on PDM filters.

One of the goals of the EOS measurement research effort that motivated the current study was to evaluate the efficacy of using a portable spectrometer to measure silica (α -quartz) on filter samples collected during the shift, to provide timely feedback to miners regarding their

exposure to silica-rich dusts. Logical choices for such a measurement method are X-ray diffraction (XRD) and FT-IR spectrometry, since current mining regulations are enforced based on laboratory methods employing these techniques. XRD has the advantage of being crystalline-specific, and can differentiate between the different forms of quartz i.e., α -quartz, β -quartz, and amorphous silica. It also provides a greater number of alternative peak locations in the measured diffractograms than FT-IR spectrometry, which can potentially help in differentiating interfering materials. FT-IR spectrometry, while not specific to the crystallinity of α -quartz, was adopted for estimation of α -quartz in coal mines. It is more cost effective and simpler to use than XRD, but has the drawback of being more sensitive to confounders in the form of other siliceous minerals. However, since few siliceous minerals are found in coal mines other than α -quartz and some clays, IR spectrometry was chosen as the technique of choice for enforcing coal mine regulations. For these reasons, as well as its potential for portability, it was chosen for this study.

A field-portable FT-IR spectrometer operated in transmission mode was investigated previously and shown to be effective in measuring silica in dusts deposited on polyvinyl chloride (PVC) filter media.^(14,15) In the current study we have investigated alternative approaches, with potential for analyzing samples that are not amenable to transmission spectrometry, including the filters used in the PDM.

IR spectra of dust samples collected on certain types of filters can be acquired in two other modes besides transmission, namely attenuated total reflection (ATR), and diffuse reflection (DR) spectrometry.^(16,17) For ATR spectrometry, the evanescent wave only interacts strongly with the top 1 or 2 μm of the sample. Since the collected dust particles can be as large as 4 μm in diameter and multiple layers can potentially deposit on the filter, much of the deposited dust would not be interrogated by the evanescent wave. Indeed, in preliminary experiments, [A. L. Miller, unpublished results (2012)], ATR was found to be useful only for very lightly loaded filter samples (< 2 μm in average sample thickness).

Samples investigated by mid-infrared DR spectrometry are typically thicker than the beam penetration depth so that they fulfill the “infinite depth” criterion, i.e., samples for which an increase in thickness does not lead to a change in the diffuse reflectance. The effective depth of penetration is dependent on several variables including the mean diameter of the particles and the absorptivity of the band(s) under consideration, and can vary from a few micrometers for very strongly absorbing samples to more than 1 mm for transparent powders such as KBr.⁽¹⁸⁾ Because the samples of mine dusts that are collected on filters are usually only a few micrometers thick (vide infra), the “infinite depth” criterion is rarely fulfilled. Indeed, the samples are usually so thin that scattering by the deposited powder is minimal (which is why transmission measurements of these samples are successful).

In contrast to the “dust layer,” the filters on which the samples are collected scatter the incident radiation efficiently and are usually thick enough (150–500 μm) to fulfill the “infinite depth” criterion. Thus if a filter with a layer of collected mine dust is placed in a DR accessory, the resulting spectrum will be due to transmission through the dust layer, diffuse reflection from the filter and retransmission of the diffusely reflected beam back through the dust layer, i.e., the spectrum that is measured should be considered as a

transflection spectrum rather than a DR spectrum. Transflection measurements of viscous liquids on a scattering ceramic substrate are commonly made in near-infrared (NIR) spectrometry⁽¹⁹⁾ but are rarely used to obtain mid-infrared (MIR) spectra of thin layers on diffusing substrates, since most such substrates strongly absorb mid-infrared radiation. Very thin films on flat metallic substrates are thus more commonly measured. The typical thickness that is required to give a “good” mid-infrared transmission spectrum (i.e., one where the peak absorbance of the strongest band(s) is between 0.5 and 1.5) is 10–20 μm for most pure materials and the thickness of the deposited samples is usually considerably less than this. Thus the “diffuse transflection” spectrum of mine dusts deposited on weakly absorbing, but strongly scattering, filters such as the PVC filters used in this and previous work⁽²⁰⁾ should allow the thickness and the concentration of α -quartz in the dust sample to be obtained. Unlike DR measurements of “infinitely deep” samples, the infrared beam in diffuse transflection spectrometry passes through the entire thickness of the deposited dust and hence the accuracy of this method will not be affected by layering.

DR spectrometry has some limitations, as described in earlier works.^(21,22) The technique depends, in part, on scattering of the incident radiation within the dust layer, which can be affected by layer thickness, particle size, and packing density. The signal also has a component that is derived from specular reflection from the sample surface and, for thin layers of the analyte, reflection from the substrate on which the dust is trapped. There are two classes of accessories for DR spectrometry: those in which the radiation collected from the sample is on the same axis as the incident beam and those where the radiation is collected off-axis. In the former design, more of the specularly reflected light is collected which can affect the linearity of Beer's law plots (vide infra).⁽¹⁷⁾ The accessory used in this study has an off-axis optical design. Although particle size has been shown to affect signal intensity,⁽²³⁾ in this study the effect of particle size was neglected since all samples were from the same source and all were collected using a cyclone pre-selector which removed most of the larger particles for which front-surface reflection would be expected to be large.

In this article we report the results of a study to evaluate mid-infrared DR spectrometry as a viable analytical technique for α -quartz on coal-dust-laden filters. The research approach is based on the initial success in measuring α -quartz on 37 mm PVC filters, using a portable FT-IR spectrometer in transmission mode.⁽²⁰⁾ In the present study we extend that work to DR/FT-IR spectrometry, which offers the unique capability to analyze samples for which much of the IR beam is not transmitted through the substrate. This is the case for filter samples collected by a PDM, since the filter material in the PDM is adhered permanently to a polypropylene filter holder, by which the IR beam is strongly attenuated.

Another hurdle to analyzing PDM filters is that the filters used in the current PDM are fabricated from borosilicate fiber-glass, and it was expected that strong front-surface reflection (reststrahlen) from the more intense Si-O stretching bands in the spectrum of the fiberglass would lead to interference in DR measurements. The borosilicate fiberglass filters are also incompatible with the MSHA P7 analytical method,⁽²⁴⁾ an issue previously addressed by NIOSH research.⁽⁹⁾ While the borosilicate filters do not contain crystalline silica, the fact that the siliceous content of the filter is not removed when the sample is ashed presents a potential source of interference during analysis for α -quartz. NIOSH researchers

therefore demonstrated the efficacy of a novel filter medium for the PDM, a polyester-backed nylon fiber filter.⁽⁹⁾ The nylon filter material and the original borosilicate material were incorporated into the current study, as well as PVC filters of the type that were used in a previous study in which transmission spectra were measured and analyzed.⁽¹⁴⁾

The aim of this study was to determine whether a field-portable FT-IR spectrometer operated in DR mode is capable of detecting small amounts of α -quartz (around 25–200 μg per filter) in RCMD deposited on filters, and whether it can differentiate α -quartz from potential IR-confounders in the coal dust (primarily kaolinite). The applicability of the method was evaluated using respirable samples of α -quartz, kaolinite, and coal dust. The method was first determined to be applicable using samples deposited on 37 mm PVC filters as in the previous study where FT-IR was used in the transmission mode.⁽¹⁴⁾ The applicability of the method to nylon filters was then evaluated, as well as the amenability for analyzing mine dusts deposited on the current borosilicate fiberglass PDM filters.

MATERIALS AND METHODS

Materials and Sample Preparation

Min-U-Sil 5 (henceforth referred to as “Minusil”), which is a standard source of pure silica with an α -quartz content of 92%,⁽²¹⁾ was used for determining the sensitivity and the linearity of the correlation between silica mass and spectra acquired on the portable FT-IR spectrometer. Since measurement of silica in coal dust by IR spectrometry typically requires a correction for the presence of kaolinite⁽¹²⁾ a well-characterized source of Georgia kaolinite was also chosen and analyzed. The dust was similar to that chosen in previous research in which the consistency of IR signals for various types of kaolinite was investigated.^(25,26) The type of coal dust used in this study was characterized previously⁽¹⁰⁾ and is termed “Pittsburgh 4” (P4) dust. It was derived from the Pittsburgh coal seam and ground to a mean target diameter of 4 μm .

All dusts were aerosolized at ambient conditions using a fluidized bed aerosol generator (TSI Inc., Shoreview, MN) and collected onto filters using a Marple chamber. Note that for this study, all dust samples were collected downstream of a Dorr-Oliver (DO) cyclone, (50% cutoff size of 4 μm), and the estimated mean particle diameter was about 1 μm . Analysis by the P7 method of P4 dust samples similar to those used in this study, yielded fractions for α -quartz and kaolin of approximately 5.5% and 20.6% by weight, respectively. While the silica content of the samples was constant, the standard deviation of the P7 data was $\pm 0.32\%$, which indicates the precision of that method is about 6%.

Two types of samples were investigated. For the first type, dust was collected onto 14 mm or 37 mm diameter filters mounted in polystyrene cassettes, using a flow rate of 1.7 LPM. For the second, dusts were collected using multiple PDMs, which were placed inside the Marple chamber, each containing a 14-mm filter, permanently mounted onto a polypropylene holder. The PDMs were started simultaneously and each drew air through its PDM filter at a flow rate of 2.2 LPM. For both cases, the filters were preceded by DO cyclones with a 50% cutoff size of 4 μm . By definition the cyclones produce respirable dust samples, so all further mention of dust samples in this article assumes they are respirable.

Three types of filter material were used in this study (Figure 1). The first type was fabricated from PVC, which is commonly used for collecting dust samples and is known to be a good medium for IR transmission analysis.⁽²⁰⁾ The second filter material used was fabricated from borosilicate fiberglass and woven glass fabric with a poly(tetrafluoroethylene) binder and is subsequently referred to as a borosilicate fiberglass filter; this material is currently used as the filter in PDMs.⁽⁹⁾ The third type was an ashable polyester-backed nylon fiber filter material that is in development by NIOSH to provide an appropriate filter for lab-based IR quantification of α -quartz on PDM filters by the P7 method.⁽⁹⁾

For method evaluation, four sets of filter samples were collected. Three sets of samples were collected onto 37 mm diameter PVC filters, using aerosolized dust from coal, Minusil, and kaolinite. One set of aerosolized coal-dust samples was collected onto 14 mm nylon filter material. For these four sample sets, gravimetric analysis was conducted on the filters to provide known mass loadings.

Two additional sample sets were collected using aerosolized coal dust. The samples were collected on two types of PDM filters, namely borosilicate fiberglass and nylon filters. Samples were collected using the current version of the PDM (Thermo Scientific Model 3600) placed directly into the Marple chamber, and the mass of dust was determined directly from the PDM user interface, which has been previously proven to accurately reflect gravimetric mass.⁽¹⁰⁾ Note that for these two sample sets, the filters were permanently adhered to the polypropylene holder. In summary, the six types of samples used in this study, employing three different types of filter material, are listed in Table I.

Samples were loaded in the range of 100–5300 $\mu\text{g}/\text{filter}$, depending on the type of dust and size of filter. Since different sized filters were used, the loading was also expressed as $\mu\text{g}/\text{mm}^2$. For reference, Table II gives examples of some filter loadings expressed in both ways, as well as the equivalent airborne concentration that would result in each loading, based on an 8-hr sample.

Analytical Method/IR Spectroscopy

Because different functional groups absorb at characteristic wavelengths in the infrared spectrum, IR spectroscopy is commonly used to determine the molecular composition of a sample. Today, most IR spectra are measured by FT-IR spectrometers in light of their speed, sensitivity, and photo-metric accuracy.^(17,27) For the DR measurements described in this article, the ratio of the single-beam spectra of the filter sample and a blank (control) filter is calculated, yielding the reflectance, $R(\tilde{\nu})$, at each wavenumber, $\tilde{\nu}$. In transmission spectrometry, where the equivalent operations yield the transmittance spectrum, $T(\tilde{\nu})$, quantitative determinations are made after converting the transmittance spectrum to the absorbance spectrum, $A(\tilde{\nu})$, by the operation:

$$A(\tilde{\nu}) = -\log_{10} T(\tilde{\nu}) \quad (1)$$

For a single component that is in a non-absorbing matrix, $A(\tilde{\nu})$ is proportional to the product of the concentration of the analyte, c , and the path-length of the cell, b , with the constant of proportionality being the absorptivity, $a(\tilde{\nu})$,

$$A_i(\tilde{\nu}) = a_i(\tilde{\nu})bc \quad (2)$$

where $a_i(\tilde{\nu})$ has the units of $(\text{concentration} \cdot \text{pathlength})^{-1}$; this is usually known as Beer's law. For N -component mixtures where more than one component absorbs at $\tilde{\nu}$, the total absorbance is given by:

$$A(\tilde{\nu}) = \sum_{i=1}^N (a_i(\tilde{\nu})bc_i) \quad (3)$$

Band intensities in the DR spectra of samples of “infinite depth” are best described by the Kubelka-Munk function, $f[R(\tilde{\nu})_\infty]$, or $(1 - R(\tilde{\nu})_\infty)^2/2R(\tilde{\nu})_\infty$, where $R(\tilde{\nu})_\infty$ is the diffuse reflectance of an “infinitely thick” sample. For thick, dilute powdered samples in mid-IR DR spectra, $f[R(\tilde{\nu})_\infty]$ is linearly proportional to the concentration of the analyte. Since the spectra of thin layers on a diffusing substrate do not fulfill the “infinite depth” criterion, and are more analogous to transmission spectra, we have converted all spectra to $-\log_{10}R(\tilde{\nu})$ for this study. Although for scattering samples, $-\log_{10}R(\tilde{\nu})$ is not theoretically proportional to concentration, it is a good approximation, especially for thin samples. In this article we will refer to $-\log_{10}R(\tilde{\nu})$ as the absorbance at $\tilde{\nu}$, even though it is more accurately called the pseudo-absorbance. For thin layers on a diffusing substrate, scattering is minimal. Thus the height or area of the bands in $-\log_{10}R(\tilde{\nu})$ spectra is approximately proportional to the amount of each component that is present in the sample, i.e., the product of path-length and concentration.

Sample Analysis

The instrument used was a Bruker Alpha FT-IR Spectrometer equipped with a “QuickSnap” module for DR spectrometry (Bruker Optics, Billerica, MA). All spectra were measured at a resolution of 4 cm^{-1} to match previous IR analyses, where it was found that a higher resolution causes degradation in the signal-to-noise ratio (SNR).^(17,20) Samples were placed face down in the DR module with the center of the filter directly over the sampling window (Figure 2). A lid with a hole centered over the sample window was then pulled down to cover the sample, and a gold-mirrored backing plug was placed through the hole and up against the back of the filter. Because of the small beam diameter (6 mm) in the DR accessory being used in this work, only a localized circular region of $\sim 28\text{-mm}^2$ area near the filter center was examined. This area has been shown to be representative of the entire filter, allowing for reasonable empirical calibration of the method for a range of sample types and filter loadings.^(20,28)

The reflectance spectrum, $R(\tilde{\nu})$, was calculated by ratioing the single-beam spectrum of the sample against that of the blank filter. While this was done for consistency, the disadvantage of this approach for DR analyses is that as the layer depth increases, the contribution from the filter will be reduced, yielding possible over-correction for the filter absorption bands. The layer thickness was estimated using sample mass, deposition area, and an approximated

bulk density for the dust. The average thickness was estimated to be less than 5 μm for most cases and, with the exception of the fiberglass filters where specular reflection at the strongest substrate bands is high, this procedure appeared to have a negligible effect on the results.

The most characteristic (albeit not the strongest) absorption of α -quartz is a pair of bands at 800 and 780 cm^{-1} ,⁽¹²⁾ as well as a relatively weak band at 1870 cm^{-1} .⁽²²⁾ While it has been shown that DR-based quantification of α -quartz can be accomplished using the 1870 cm^{-1} band,⁽²⁹⁾ some of the spectra generated in this study did not present a detectable peak at this wavenumber, so no calibration data based on that peak were available for samples where the α -quartz concentration was low. However, kaolinite has important absorption bands at 915 and 800 cm^{-1} , the latter of which interferes with the α -quartz band at 800 cm^{-1} .

Each spectrum was linearly baseline corrected between 816 and 767 cm^{-1} and integrated between these wavenumbers. The points used for baseline correction of the kaolinite bands were 930 and 900 cm^{-1} for the 915- cm^{-1} band and 816 and 767 cm^{-1} for the (interfering) 800- cm^{-1} kaolinite band measured in the absence of α -quartz.⁽²⁰⁾ For the coal dust samples on nylon filters, these points were adjusted to 825 and 790 cm^{-1} due to the unique shape of the spectra caused by background interference.

As for previous work on transmission spectroscopy of similar samples,⁽²⁰⁾ DR spectra of the samples collected on PVC filters were measured by averaging 40 scans (in less than 1 min). Since attenuation by nylon and borosilicate fiberglass filters was high, the DR spectra of samples on these filters were measured with 120 scans (about 2 min) in an attempt to improve the SNR.

Spectra of the three filter types, generated using the single-beam spectrum measured with a diffusing gold plug as the analytical background, were examined to assess potential suitability, particularly the region of interest where α -quartz absorbs (Figure 3). We note that the diffuse reflectance of the gold plug decreases at longer wavelength; thus it appears that the baseline of the PVC spectrum is lower at long wavelength than it might have been, had a more appropriate reference been available to us. The blank PVC filters had no backing, while the nylon and borosilicate filters were mounted on polypropylene PDM filter holders. The nylon filters had a thin polyester backing layer as well. It can be seen that the fiberglass filter has very high absorption in the region below 1400 cm^{-1} and appears to be unsuitable for these measurements. The DR spectrum of the nylon filter shows strong absorption below 1700 cm^{-1} . The C=O stretching band of an aromatic polyester at ca. 1720 cm^{-1} is not observed in the measured DR spectrum, indicating that the diffusely reflected beam has not penetrated down to the polyester backing. Several strong sharp bands are present in the spectrum near 800 cm^{-1} (the region of the α -quartz doublet) which would be expected to deleteriously affect the DR spectrum when used for the quantification of α -quartz. Thus neither the borosilicate fiberglass or nylon-fiber filters should be considered as suitable substrates for DR measurements of quartz in filter-deposited dust. In comparison, the spectrum of the PVC filter has very low absorption below 1200 cm^{-1} and a window at about 800 cm^{-1} , making it well-suited to the application at hand.

Notably addressed in this study was the issue of the uniqueness of PDM filters, i.e., the fact that the borosilicate fiberglass and nylon fiber filters are permanently affixed to the polypropylene filter holder using a thin outer ring and a sonic welding process that binds all the parts together (Figure 4). The central aperture that connects the filter to the PDM inlet is less than 1.8 mm² in area and partially obstructs the IR beam, making transmission measurements nearly impossible. This is the motivation for evaluating DR spectrometry for this application.

Measurement of α -quartz by analysis of the DR spectra from coal-laden nylon and fiberglass PDM filters presented a challenge that is not present when samples on non-PDM filters are analyzed, namely the possibility of interference from the borosilicate fiberglass and nylon filter materials used in the existing PDM filters since both materials strongly absorb IR radiation as noted in the previous paragraph.

The determination of α -quartz in coal dust on the 14 mm nylon filters was carried out to replicate the size of current PDM filters, while eliminating one variable, namely the presence of the polypropylene filter holder. The interference derived from the polypropylene filter holder was evaluated by analyzing “free” 14 mm nylon filters (without filter holder) and then the nylon PDM filters, and comparing the results. The integrated absorbance of the 800 cm⁻¹ doublet was plotted against the coal dust mass loading for both types of samples, and the difference attributed to the presence of the polypropylene filter holder. This comparison has the limitation that two different methods were used to estimate the mass loading on the two types of 14 mm filters. The mass of the “free” filter samples was measured gravimetrically, while that of the PDM samples was taken from the PDM logged data. For both types of samples, the mass of α -quartz was estimated using the average percent of α -quartz in the coal samples as determined from P7 data.

RESULTS AND DISCUSSION

Measurement of Silica on 37 mm PVC filters

To determine the applicability of DR spectrometry for quantifying thin layers of quartz dust, five samples of Minusil were prepared on 37 mm PVC filters, with masses of α -quartz in the range of 100–600 μg (0.1–0.6 $\mu\text{g}/\text{mm}^2$). The integrated area of the 800 cm⁻¹ doublet for each sample was plotted against mass of α -quartz deposited per unit area of the filter (Figure 5). The correlation is linear, with no decrease in the signal at higher loadings, suggesting that the effect of varying layer thickness is negligible for such thin layers and confirming that silica samples loaded in this manner are easily quantified.

For Figure 5 and subsequent graphs, loading of the filters is expressed as mass per unit area, allowing for ease of comparing analyses on filters of different sizes.

Measurement of Kaolinite on 37 mm PVC filters

Since the IR spectrum of kaolinite has an absorption band at 790 cm⁻¹ that interferes with the determination of quartz involving the 800-cm⁻¹ doublet,^(12,30) a kaolinite correction scheme was developed that entails measuring the area of the kaolinite band at 915 cm⁻¹ for

a standard kaolinite material and using a calibration factor to estimate the area of the masked kaolinite band at 790 cm^{-1} .^(13,25)

To confirm that the ratio of the two bands is constant in DR spectra, the area of the kaolinite band at 790 cm^{-1} was plotted against that of the band at 915 cm^{-1} for ten samples of Georgia kaolinite over the expected range of mass loadings found in mines. The linearity ($R^2 = 0.99$) of the data (not shown) indicated that a potential peak ratio calibration factor would be consistent at all loadings, confirming that the kaolinite correction technique described above would be valid for DR measurements. This also confirmed that for the purposes of this study, the effect of kaolinite on the 800 cm^{-1} doublet would be consistently proportional to mass loading, and therefore kaolin correction could be omitted for the coal samples used in this study without introducing a measurement bias.

Measurement of Silica in Coal Dust on 37 mm PVC filters

A coal dust sample containing a given amount of α -quartz, typically 1–6% by weight⁽⁵⁾ will have a thicker dust layer than a pure quartz (Minusil) sample with the same mass of α -quartz. For DR analysis of thin dust layers, much of the incident IR beam will penetrate through the sample and will be diffusely reflected from the underlying filter material, while for the analysis of thick layers a smaller fraction of the incident beam will penetrate through the sample and reach the filter material.⁽¹⁸⁾ This suggests that the amount of α -quartz quantified by DR spectrometry in Minusil on a filter will not be proportional to that quantified for an equivalent amount of silica in coal dust, unless the coal dust layer is very thin. For coal dust layers thicker than about $10\text{ }\mu\text{m}$, the calibration curves relating absorbance to mass loading for the (much thinner) Minusil samples can therefore not be used to estimate the mass of α -quartz in the coal dust samples as was done previously using transmission IR spectrometry⁽²⁰⁾ For this reason, in the present study we used calibration curves derived from coal samples.

To develop an α -quartz calibration curve using coal samples, 20 samples of P4 coal dust on 37 mm PVC filters were analyzed in a manner similar to the determination of Minusil described above. The spectra were first divided into a calibration set (13 samples) and a validation set (7 samples), using a semi-random approach to sample selection that ensured both sets effectively spanned the loading range. For the 13 calibration samples, the area of the 800 cm^{-1} silica doublet was plotted against mass loading of coal ($\mu\text{g}/\text{mm}^2$) to generate a calibration curve (data not shown). Using the resulting calibration equation, the masses of α -quartz ($\mu\text{g}/\text{mm}^2$) in all samples were estimated (Figure 6). The slope of this plot reflects the percent of α -quartz in the dust, which was constant (and known) for all samples of this well-characterized dust.⁽¹⁰⁾

The 20 P4 coal samples were loaded in the range of 2800–5300 μg , which is higher than the levels expected in coal mines (1000–2000 μg).⁽²⁰⁾ There were two reasons for choosing such high mass loadings. First, the NIOSH methods manual suggests using an upper value at least twice as great as the expected value in the field and, secondly, it is known from experience that field samples can sometimes contain such heavy amounts of dust, and we wished to know whether our data would still be valid (linear calibrations would still hold) at such high loadings. In spite of the fact that the samples were heavily loaded, the DR analysis gave a

fairly good correlation between estimated versus known α -quartz mass, yielding for the validation samples a slope of 1.06, and an R^2 value of 0.91 (data not shown). The root mean square error of prediction (RMSEP) was slightly smaller ($0.017 \mu\text{g}/\text{mm}^2$) than the root mean square error of calibration (RMSEC) ($0.020 \mu\text{g}/\text{mm}^2$), presumably because the size of both data sets was small. If samples loaded above $\sim 4,000 \mu\text{g}$ were omitted from the validation set, the R^2 value increased to 0.94, while the slope changed only slightly (data not shown). These data suggest that DR analysis of silica in coal dust deposited onto 37 mm PVC filters is comparable to analysis of similar samples measured by transmission (correlation coefficients of 0.91 vs. 0.94),⁽¹⁵⁾ especially at loadings expected in the field ($<4,000 \mu\text{g}/\text{filter}$ or $\sim 4.16 \mu\text{g}/\text{mm}^2$ for a 37 mm filter).

Measurement of Silica in Coal Dust on 14 mm nylon filters

To test the applicability of analyzing α -quartz in coal dust deposited on PDM filters, coal dust samples on 14 mm nylon filters (initially not mounted on PDM holders) were first analyzed, to investigate the possible effects of the filter holder on DR analyses. Thirty nylon filters, containing coal dust loaded in the range of 700–2400 $\mu\text{g}/\text{filter}$, were analyzed and the integrated areas were used to calculate a linear calibration curve representing the correlation between the area of the 800 cm^{-1} doublet and the known coal (and thus the α -quartz) mass loading (Figure 7). The data were divided into a calibration set (20 samples) and a validation set (10 samples), employing a semi-random approach as above. Using the resulting calibration equation, the mass of each sample was calculated (Figure 7). The results suggest that the correlation is linear, although the R^2 value of 0.90 is not as good as for Minusil. This result is not unexpected since there is less precision in the determination of the percent α -quartz in the coal dust than in the gravimetric weighing of Minusil.

While the coal dust samples deposited on the 14 mm nylon filters had lower masses than those deposited on the 37 mm PVC filters, the mass per unit area was greater. In spite of this, the DR analysis yielded a reasonably good correlation with coal mass, with an R^2 value of 0.90, and the root mean square error of calibration (RMSEC) and prediction (RMSEP) were calculated as $0.11 \mu\text{g}/\text{mm}^2$ and $0.086 \mu\text{g}/\text{mm}^2$, respectively (data not shown). Similar to the data for PVC filters, when the two higher loadings (six data points) were removed from this data set, the R^2 value increased to 0.94 (data not shown). Although the small number of samples limits the statistical power of this set of measurements, the data suggest that DR analysis of coal dust deposited onto 14 mm nylon filters is reasonably accurate when the filter is not mounted on the PDM filter holders, especially at loadings below about $2 \mu\text{g}/\text{filter}$.

A similar but smaller set of samples was prepared using nylon filters mounted in the PDM holders. Three nylon PDM filter samples were analyzed and the data were used to generate a calibration curve. To compare the results with those of the nylon filter material not in the PDM holders, the raw data for both experiments were plotted together (Figure 8). Analyses made when the filter is mounted on the holder have a reduced signal, and while the small size of the sample set limits the ability for a dependable correlation, it appears that the signal begins to drop off for loadings above about $7 \mu\text{g}/\text{mm}^2$ ($1000 \mu\text{g}/\text{filter}$). Since the IR response

dropped off at loadings less than those expected in field samples, no further analyses were conducted on these data.

Measurement of Silica in Coal Dust on borosilicate fiberglass PDM Filters

DR analysis of coal dust on the borosilicate fiberglass PDM filters produced spectra with considerable noise and poor repeatability in the peak shape and area of all bands, including the region around 800 cm^{-1} , as compared to those for the nylon PDM filters (spectra not shown), suggesting that DR spectrometry cannot be used to obtain repeatable results from borosilicate fiberglass PDM filters. This conclusion was confirmed in subsequent analyses of coal-dust-loaded borosilicate fiberglass PDM filters for which very poor correlation between the area of the 800-cm^{-1} doublet and the mass of coal dust deposited was observed (Figure 9). The effect of the siliceous content in the filter results in a very poor linearity ($R^2 = 0.19$) indicating that dependable correlation between measured peak areas and coal mass (and thus α -quartz mass) is not possible.

CONCLUSION

An advantage of using DR spectrometry for analyzing filter samples is that the beam penetrates through the dust sample, but does not need to pass through the filter or the backing material. Despite some limitations, DR was shown to produce results similar to those using the transmission mode for quantification of quartz on PVC filters, when the filters are loaded with up to $\sim 11\ \mu\text{g}/\text{mm}^2$ ($\sim 3500\ \mu\text{g}$ on a 37-mm filter) of coal dust. Most of the observed limitations were caused by the use of an upward-looking DR accessory and the nature of the existing PDM filter holder. With appropriately designed DR optics and filter mount, along with use of PVC filters, these limitations should no longer exist.

DR analysis of silica in coal dust loaded onto 14 mm nylon fiber filters showed a linear correlation similar to the measurements made on PVC filters, up to a mass loading of around $14\ \mu\text{g}/\text{mm}^2$ ($2000\ \mu\text{g}$ on a 14 mm filter), after which the response dropped off slightly. However, when the nylon material was mounted on PDM holders, the DR signal was reduced. With the borosilicate fiberglass filters, even smaller signals resulted. The investigation described above could be criticized because only one source of P4 coal was used for all measurements. However, recent results obtained by transmission spectrometry in our laboratory with more than a dozen coals of different rank, α -quartz, and kaolinite content, showed that the predicted concentrations of α -quartz were close to the known values, provided that the spectra were processed using the chemometric techniques that we described recently.⁽¹⁵⁾ Since the results reported above showed approximately the same accuracy as the corresponding measurements previously performed using transmission spectrometry, there is good reason to expect that equally high accuracy could be obtainable by DR spectrometry, and with less sample handling.

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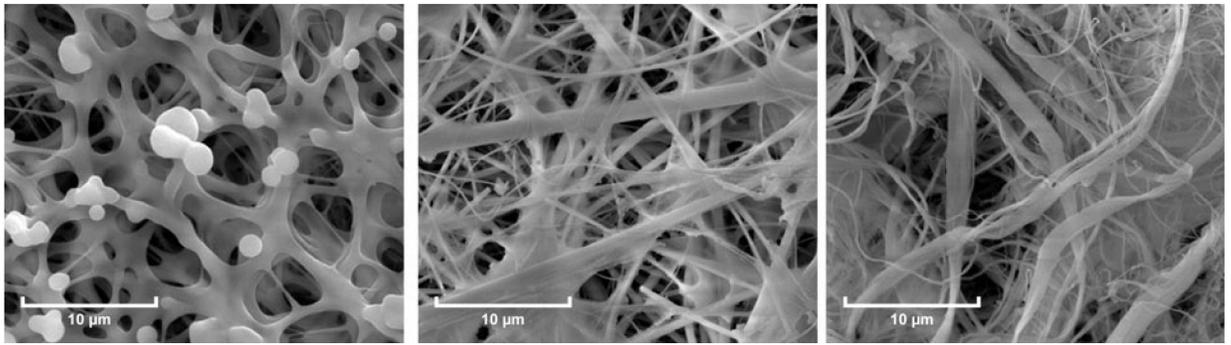


FIGURE 1.
SEM images (at 5000X) of the surface topography for the three filter materials: a) PVC, b) Borosilicate fiberglass, and c) Nylon.

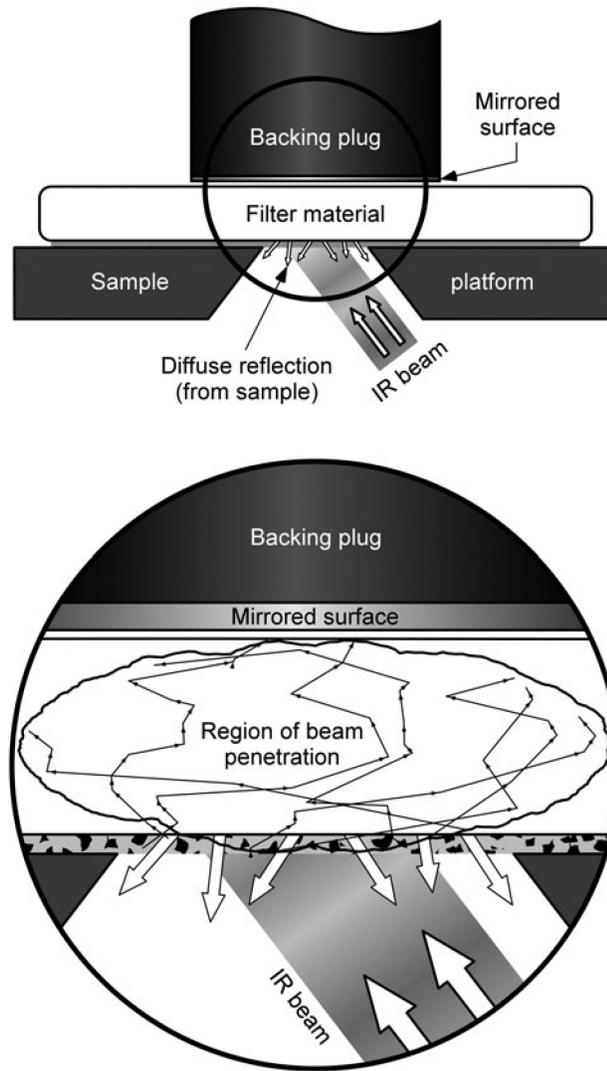


FIGURE 2. Artist sketch (not to scale), showing relative geometry of sample placement and beam interaction with the sample.

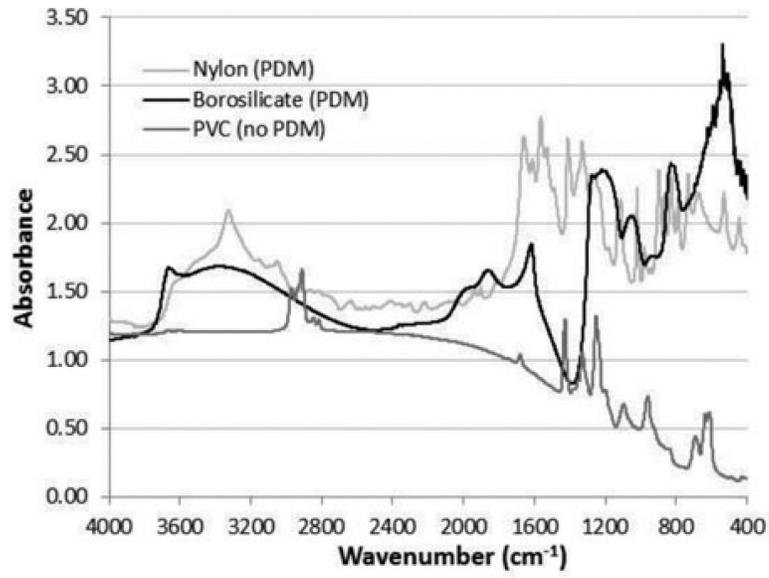


FIGURE 3. DR spectra of nylon (ashable), borosilicate fiberglass, and PVC filters. (The first two were mounted on polypropylene PDM filter holders).



FIGURE 4.
a) Borosilicate fiberglass filter mounted on a 14 mm PDM filter holder. b) Magnified image of a filter holder, showing raised spokes and 1.8 mm diameter central exit port, obstructed by structural bar. Note that some PDM filter holders are white, due to trace amounts of TiO_2 in the polypropylene formulation.

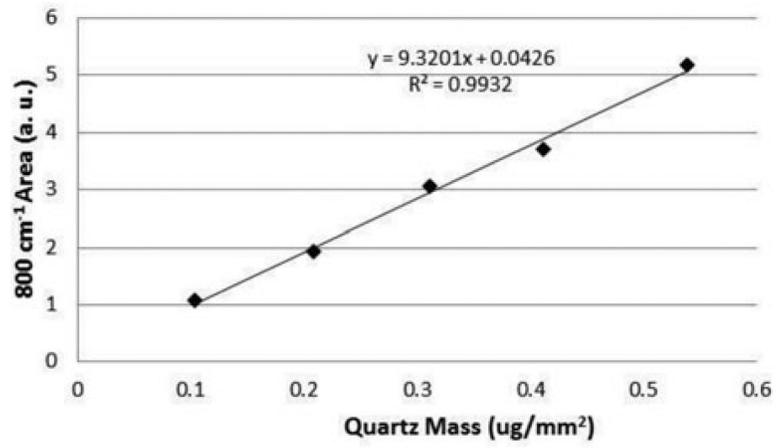


FIGURE 5. Area of doublet at 800 cm^{-1} versus gravimetric mass concentration of quartz on 37 –mm PVC filters.

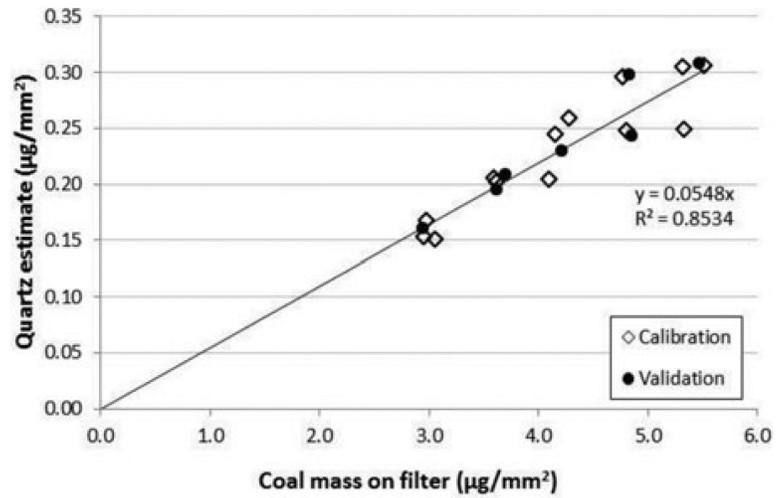


FIGURE 6. Estimated quartz mass versus actual total mass of P4 coal dust on 37 mm PVC filters loaded in the range of 2800–5300 µg/filter, using 13 calibration samples and 7 validation samples (linear fit on this graph and those in Figures 7 and 8 is for calibration samples only)

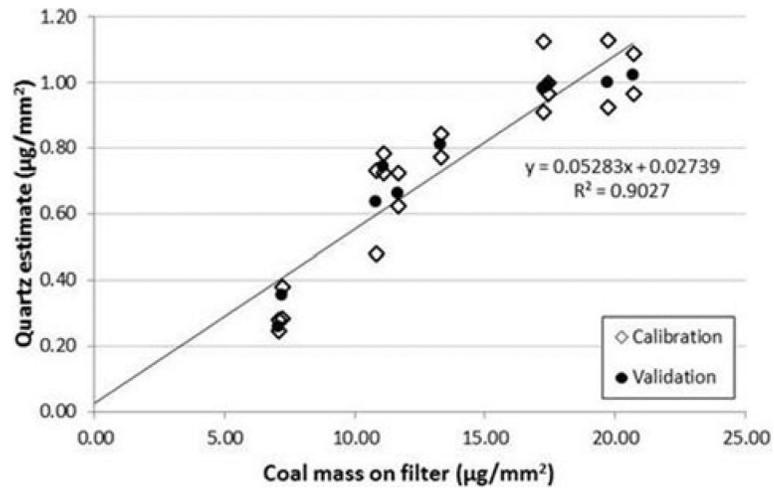


FIGURE 7.
Estimated quartz mass versus actual coal mass for 14 mm nylon filters, loaded in the range 700–2400 µg/filter

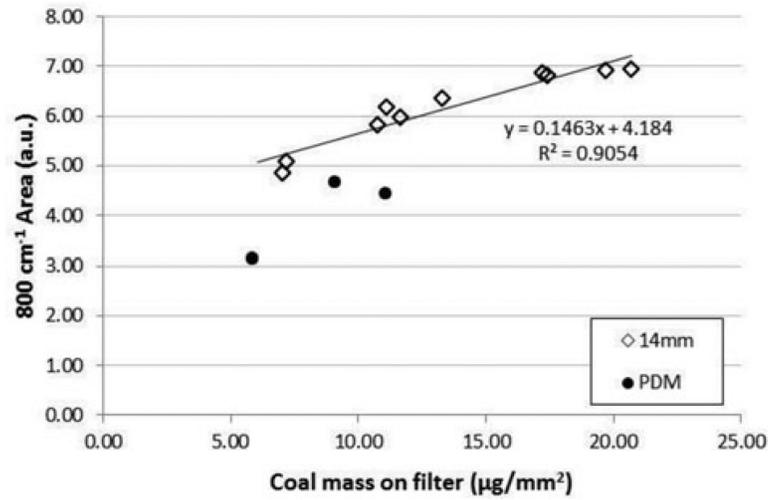


FIGURE 8. Area of the 800 cm^{-1} doublet versus coal dust mass for the nylon filter material (cut to 14 mm) and for the nylon PDM filters, loaded in the range of 700–2400 and 700–1300 $\mu\text{g}/\text{filter}$, respectively

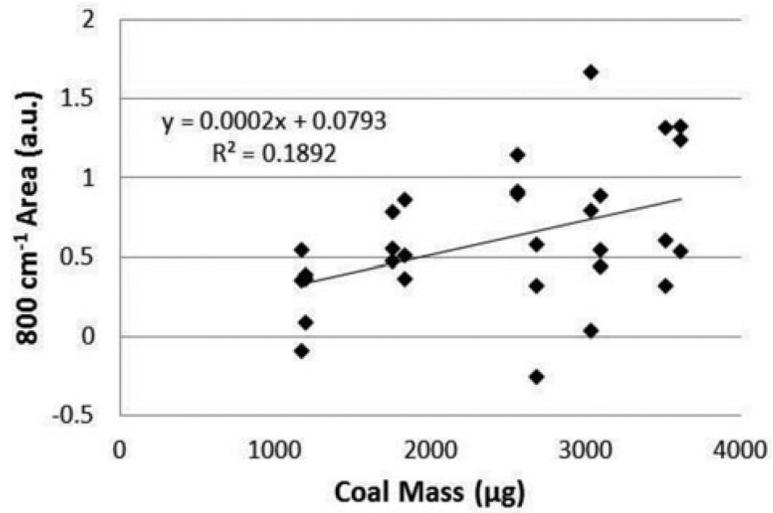


FIGURE 9. Area of silica doublet peak at 800 cm⁻¹ versus coal dust mass, for borosilicate fiberglass PDM filters, loaded in the range of 1000–3500 µg/filter.

TABLE I

Summary of Sample Types Used in This Study

Filter Size	Filter Type	Dust Type
37 mm	PVC	Minusil
37 mm	PVC	kaolinite
37 mm	PVC	coal
14 mm	nylon	coal
14 mm	nylon on PDM mount	coal
14 mm	borosilicate fiberglass on PDM mount	coal

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TABLE II

Reference Data for Filter Loading

Total Mass (μ g/filter)	14 mm Filter Loading (μ g/mm ²)	37 mm Filter Loading (μ g/mm ²)	Concentration 8-hr RCMD (μ g/m ³)
500	3.77	0.52	520
1000	7.53	1.04	1042
2000	15.07	2.08	2083
4000	30.14	4.16	4167

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