



Application Note AN M143

Direct Quantification of Coal Mine Dust Deposited on a Respiratory Filter using the ALPHA II FT-IR spectrometer

Miners face a variety of respiratory hazards while on the job including exposure to silica dust. Inhalation of dust containing respirable crystalline silica (RCS) can cause lung disease, silicosis, and cancer. Presently, over 1 million U.S. workers are routinely exposed to RCS, and each year more than 250 American workers die from silicosis. The US Mine Safety and Health Administration (MSHA) mandates the monitoring and quantification of occupational exposure to airborne silica in U.S. mines [1-2].

Currently, dust samples are collected at a mine and submitted to an accredited laboratory for RCS analysis. The time between sample collection and interpretation of the results of the analysis limits the possibility for occupational health professionals to promptly address the risk of overexposure at a mining site. In addition, the results could have little to no value in the case of a mobile mining operation, because the operation usually moves to a new location before the results are available, and the RCS concentrations might change due to variation in local geology [1].

Infrared (IR) spectroscopy and X-ray diffraction are two analytical techniques that are used for exposure assessment. IR spectroscopy is mandated for use in U.S. coal mines while powder XRD is used for

| Keywords | Instrumentation and Software |
|---------------------|------------------------------|
| Coal mine dust | ALPHA II FT-IR Spectrometer |
| Direct-on-filter | Transmission module |
| Silica measurements | OPUS/Quant 2 |

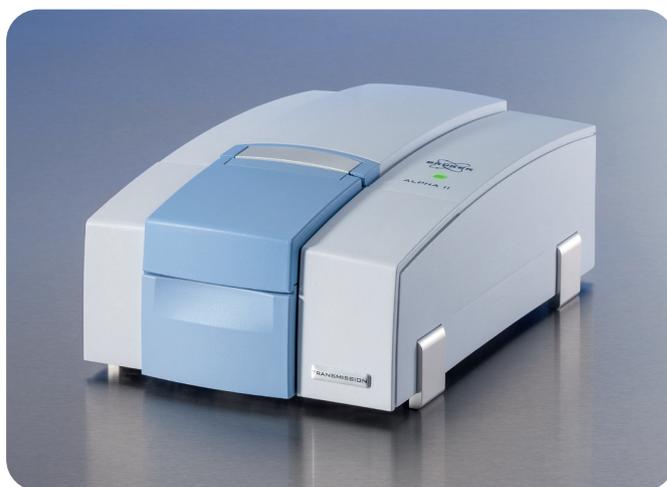


Figure 1: ALPHA II FT-IR spectrometer with transmission module.

evaluation of non-coal mine dusts. Both techniques use samples in a powder form which are acquired in a mine using the respirable sampler. Samples must be ashed before the analysis takes place. Acquiring spectra from samples collected directly on the filter (DoF) substrate would facilitate the rapid determination of α -quartz by circumventing the ashing and redeposition steps. Developing field-based monitoring techniques for RCS is a current research objective of the National Institute for Occupational Safety and Health (NIOSH)[1-4]. The regulated respirable limit in the US mining industry is set at 100 micrograms of silica per cubic meter of inhaled air, time weighted (TWA) over a full work shift. The instrument must therefore be capable of quantifying such a small amount. This application note discusses the use of FT-IR spectroscopy for DoF analysis of coal dust objects of interest.

Experimental

15 samples with different loadings of coal and silica on PVC filters were received from NIOSH. The amount of coal dust on the filters varied from 0.1 to 4 mg. The amount of silica was in the range from 3 to 231 micrograms. Spectra of coal dust samples were acquired at 4 cm^{-1} spectral resolution using the Bruker ALPHA II FT-IR spectrometer and the transmission module (ALPHA II-T, Figure 1). The acquisition time was 30 seconds per sample. Background spectrum was collected without the sample in the sample compartment.

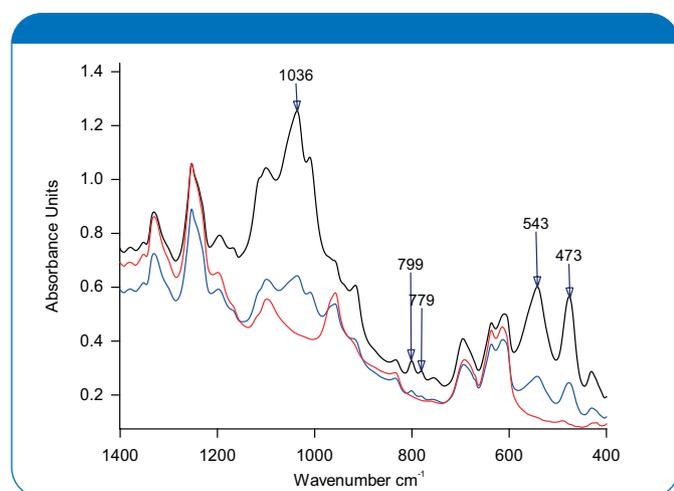


Figure 2: Spectrum of pure PVC filter (red) and filter loaded with 1.299mg coal /70 mg silica (blue), and 3.982 mg coal/230 mg silica (black).

Results and discussion

Figure 2 shows examples of spectra collected from PVC filters loaded with different amounts of coal and silica. The baseline in these spectra is tilted due to scattering from the filter surface. Two bands in the $830\text{-}760\text{ cm}^{-1}$ spectral range (sometimes called the "silica doublet") are assigned to silica in coal dust. These two bands do not overlap with bands originating from the PVC filter and can be used to quantify silica by building a calibration based on peak heights or integrated intensities of these bands. Details of such calibrations are described previously [2].

It should be noted that the IR spectra of the samples collected in this study were predominantly composed of mineral absorption bands. Spectra of certain types of coal (e.g. anthracite) show strong bands between 900 and 700 cm^{-1} due to organic material. The coal investigated in this study was ranked high-volatile bituminous and no evidence of these bands was observed. Bands at 1036 , 543 and 473 cm^{-1} are related to coal and silica. These bands considerably overlap with bands due to the PVC substrate. For this reason, the initial calibration for both silica and coal amount was created using the Partial Least Squares (PLS) model.

The PLS analysis was performed using the Bruker OPUS Quant 2 package. This package allows models to be optimized automatically. The Quant 2 software checks the common frequency regions in combination with several data preprocessing methods. The software yields only a list of used parameters such as the frequency region and the preprocessing method as well as the resulting root mean square error of cross validation (RMSECV) value and rank. The user is still responsible for choosing the best parameters for the validation. It was found that first derivative plus vector normalization within the $1485\text{-}405\text{ cm}^{-1}$ spectral range was optimal for processing this data set.

Figure 3 shows the cross-validation results for coal and silica. Even such a small sample set yields an accurate calibration with the coefficients of determination (R^2) equal to 95.61 for the coal and 97.13 for the silica. This limited sample data set shows that the Bruker ALPHA II-T units can perform the transmission spectral analysis of coal dust samples. Detailed analysis with a bigger data set is described in [3,4].

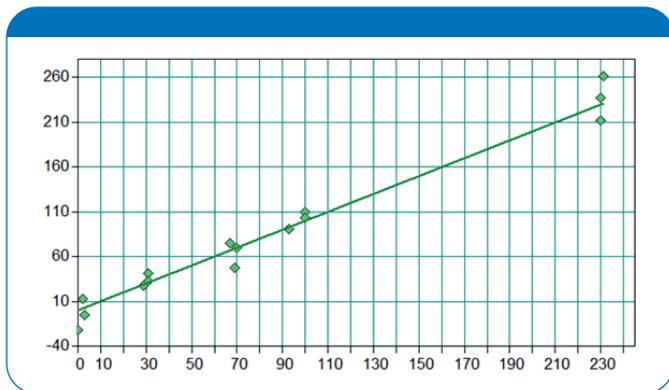


Figure 3a: Cross validation prediction vs. true for silica.

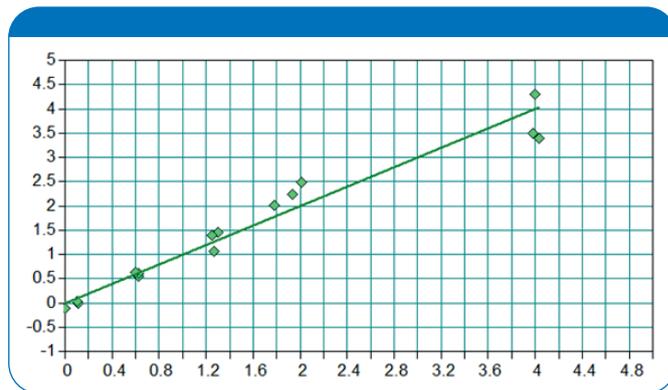


Figure 3b: Cross validation prediction vs. true for coal.

Conclusion

The Bruker ALPHA II-T spectrometer can be used for quantitative analysis of coal and silica in coal dust deposited on the PVC filter. The high sensitivity of this method allows for fast quantification of silica below the regulated respirable limit (100 micrograms/m³ TWA).

References

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