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Original Article

# Application of a Fourier Transform Infrared (FTIR) Principal Component Regression (PCR) Chemometric Method for the Quantification of Respirable Crystalline Silica (Quartz), Kaolinite, and Coal in Coal Mine Dusts from Australia, UK, and South Africa

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## Abstract

This article describes the approach used to assess the performance of a Fourier transform infrared (FTIR) and principal component regression (PCR) chemometric method when measuring respirable quartz, kaolinite, and coal in samples from a variety of mines from different countries; relative to target assigned values determined using X-ray diffraction (XRD). For comparison, FTIR results using the partial least squares regression (PLSR) method are also available. Bulk dusts from 10 Australian mines were scanned using XRD and grouped into three sets based on the levels of quartz, kaolinite, and feldspar within their crystalline mineral composition. Prediction samples were generated from 5 of these Australian mine dusts, Durrans coal dust, 2 mine dusts from the UK, and a single South African mine dust (71 samples in total) by collecting the aerosolized respirable dust onto 25-mm diameter polyvinylchloride filters using the Safety in Mines Personal Dust Sampler (SIMPEDS) operating at 2.2 l min<sup>-1</sup>. The predicted values from the FTIR chemometric methods were compared with assigned target values determined using a direct on-aerosol filter XRD analysis method described in Method for the Determination of Hazardous Substances (MDHS) 101. Limits of detection (LOD) and uncertainty values for each analyte were calculated from a linear regression between target and predicted values. The uncertainty was determined using the calibration uncertainty equation for an unweighted regression. FTIR results from PCR and PLSR are very similar. For the PCR method, the LOD for quartz, kaolinite, and coal were 5, 25, and 71 µg, respectively. For quartz, an LOD

### What's Important About This Paper?

Fourier transform infrared instruments are relatively inexpensive, portable, and potentially measure many chemical agents simultaneously, including crystalline silica, but interference can limit accuracy. Accurate measurements of respirable crystalline silica are important because of their relationship with potential risk of worker ill-health. This article describes a chemometric method, a principal component regression model derived using laboratory generated samples, that reduces the influence of interference in the spectrum to determine component concentrations. The method was used to establish detection limits for crystalline silica in mine dusts, and the study demonstrated that the method can meet international performance criteria.

of 5  $\mu\text{g}$  corresponds to an airborne quartz concentration of 10  $\mu\text{g m}^{-3}$ , assuming a 4-h sampling time and collection flow rate of 2.2  $\text{l min}^{-1}$ . The FTIR measurement met the expected performance criteria outlined in ISO 20581 when sampling quartz for more than 4 h using a flow rate of 2.2  $\text{l min}^{-1}$  at a concentration of 0.1  $\text{mg m}^{-3}$  (100  $\mu\text{g m}^{-3}$ ), the current workplace exposure limit in Great Britain. This method met the same performance criteria when measuring exposures at the Australian Workplace Exposure Standard (WES) concentration of 0.05  $\text{mg m}^{-3}$ , although in this case a sampling period greater than 8 h was needed.

**Keywords:** chemometrics; coal; kaolinite; limit of detection; principal component regression; quartz; respirable crystalline silica; uncertainty

## Introduction

The expanded uncertainty is a measure of the reliability of a reported value. It is calculated as the product of the combined standard deviations of all the steps that could contribute to its variability multiplied by a coverage factor (usually 2) as an estimate of the 95% confidence interval. The objective, in this work, is to assess the performance of a principal component regression (PCR) chemometric model for Fourier transform infrared (FTIR) analysis of respirable quartz, kaolinite, and coal against international performance standards for occupational hygiene methods, where there are requirements to work within specific levels of expanded uncertainty. In this article, the expanded uncertainty is derived from measurements on samples from workplace environments working with dusts from coal mines.

Crystalline silica is a generic name for minerals with the same elemental composition of silicon and oxygen ( $\text{SiO}_2$ ) but different crystal structures known as polymorphs. The quartz polymorph of crystalline silica is often present as a contaminant in coal and frequently found as a major component in the geological stratum that occurs next to coal seams.

Occupational exposure to aerosols containing respirable crystalline silica (RCS) is a major health issue. The word respirable refers to the particle size fraction that penetrates into the alveoli of the human lung (CEN, 1993). When inhaled, respirable-sized particles of crystalline silica can cause diseases like silicosis (HSE, 2003)

and lung cancer (Rushton *et al.*, 2012). High exposures to RCS can occur in mines due to the use of powered tools to access the seams and extract the coal, and the confined working space which restricts the dispersion and hence dilution of the aerosol. Coal dust itself is also a potential hazard to the health of a worker via inhalation and can cause pneumoconiosis (Ross and Murray, 2004).

In Great Britain (GB) and Australia, samples of workplace aerosol are frequently collected and measured to assess if worker exposures are below workplace exposure limits (WEL). In GB the 8-h WEL for RCS is currently 0.1  $\text{mg m}^{-3}$  i.e. 100  $\mu\text{g m}^{-3}$  (HSE, 2005b), whilst in Australia the Workplace Exposure Standard (WES) for RCS is 0.05  $\text{mg m}^{-3}$  i.e. 50  $\mu\text{g m}^{-3}$ . Samples of aerosol are obtained by drawing a volume of air through a respirable sampler and onto a filter or foam. The respirable sampler is located within the breathing zone of a worker and separates larger non-respirable particles in the sampled aerosol from the smaller respirable fraction. The most common approach is to use a cyclone sampler, where the smaller respirable particles, known as the respirable fraction, are collected onto the filter or foam from the centre of the vortex and the larger non-respirable particles, with larger masses and moments of inertia, move across the air flow and impact onto the body of the sampler. The collected respirable fraction aerosol is then analysed to determine the quantity of respirable hazardous substance (in this case quartz or coal), collected from a known volume of air.

X-ray diffraction (XRD) and FTIR are two analytical techniques that are commonly employed for the measurement of aerosol sampling filters containing RCS (Pickard *et al.*, 1985; HSE, 2014). Raman spectroscopy is also available (Zheng *et al.*, 2018; Stacey *et al.*, 2020) but is a relatively new technique for this type of analysis, and not yet widely used for routine work. Infrared analysis is used more widely than XRD because the instrumentation required is significantly cheaper, easier to use and maintain and provides a quicker analysis (less than 4 min in total). However, both XRD and Raman spectroscopy methods have greater specificity than FTIR as their measurement responses are more directly related to the crystalline structure of quartz present in the samples (Stacey *et al.*, 2021c).

Recent developments in technology have led to the miniaturization of FTIR instruments; which are now portable (Crocombe, 2018; Ashley *et al.*, 2020) and able to be carried to different locations to facilitate end-of-shift, or even end-of-task testing (Cauda *et al.*, 2016). This allows the analysis to be carried out on-site, rather than at a purpose-built laboratory, making results available more quickly and enabling more rapid implementation of any remedial action required to reduce exposures. However, the need for experienced interpretation of FTIR spectra for many workplace samples is a significant limitation on the widespread adoption of this new technology.

Infrared bands at 800 and 780  $\text{cm}^{-1}$  are measured for quartz, which is the most common polymorph of RCS. The basic structure of the crystalline unit cell of quartz consists of tetrahedral arrangements of silicon (Si) and oxygen (O) atoms. The tetrahedral arrangement of Si and O is also shared by a larger group of minerals known as silicates, which also have similar absorbance to quartz in the infrared fingerprint range between 500 and 1000  $\text{cm}^{-1}$  and so there is some absorbance which is coincident with the 780 and 800  $\text{cm}^{-1}$  wavenumbers (Foster and Walker, 1984). Therefore, some absorbance which occurs at infrared bands 780 and 800  $\text{cm}^{-1}$  may be attributable to the presence of other silicate minerals, which can affect the accuracy of results. Kaolinite is a silicate that is also a major interference in many workplace samples and is often found in dusts from coal mines (Lee *et al.*, 2013; OSHA, 2015).

Chemometric methods are computational processes that can interrogate spectra to reduce the influence of interference and correlate features in the FTIR spectrum to component concentrations. Several recent studies have explored the use of chemometric and other methods to reduce the effect of interfering minerals on the quartz measurement (Weakley *et al.*, 2014; Miller

*et al.*, 2016; Hart *et al.*, 2018; Salehi *et al.*, 2020). Two common chemometrics methods are partial least squares regression (PLSR) and PCR. Both methods are based on a principal component analysis. Only slight differences between predicted results were found between these chemometric methods, when a similar number of principal components were applied (Stacey *et al.*, 2021a).

## Methods

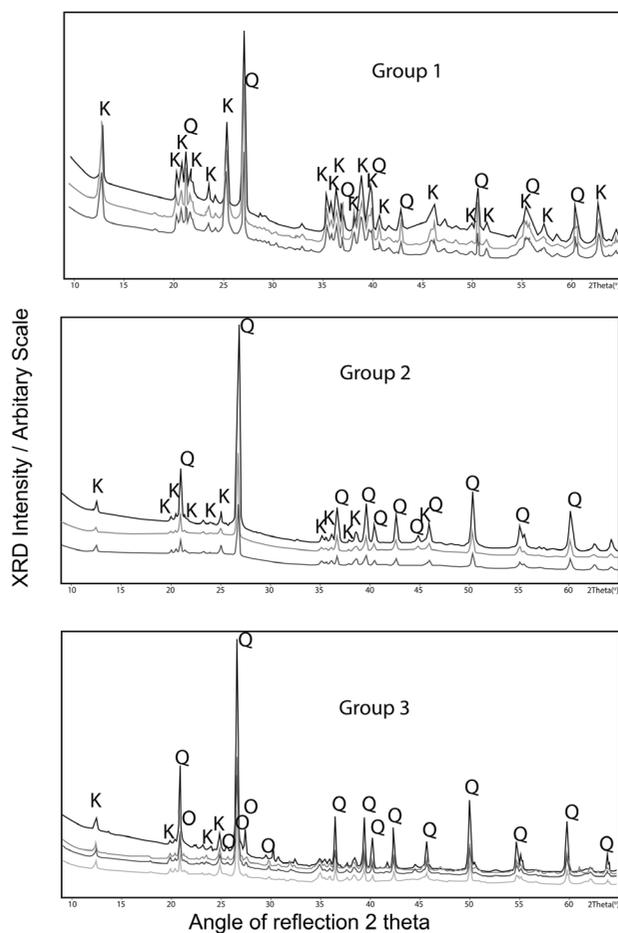
The chemometrics process requires three independent sets of samples—the calibration, validation, and prediction sets. In this study, the calibration and validation sets are based on (and extended upon herein) the preparation of samples with artificial mixtures of the three major components (quartz, kaolinite, and coal). The calibration and validation samples are mostly the same as those used in a previous study (Stacey *et al.*, 2021a). A calibration set defines the relationship between the target values and the magnitude of the vectors for principal components in their spectra. Validation samples are used to determine predicted values from the calibration and check the number of principal components with the minimum variance and the models' biases. A third set of samples known as the prediction set are used to independently challenge the model's capabilities in predicting the quantities of analytes present. To assess the potential for its universal applicability, the performance of the FTIR PCR method, calibrated using artificial mixtures of pure quartz, kaolinite, and Durrans coal dust, was evaluated when measuring samples generated from a wide variety of mine dusts. The chemometric model may over or under model the spectra and potentially produce erroneous results when the mass or proportions of analyte are outside the calibration or validation range or when mineral interferences are present that were not considered. The ability to prepare a range of mixtures with an artificial process is an advantage (when developing a model for its universal application) since these mixtures can be generated to represent the levels and combinations of significant components found in most workplace atmospheres. Quartz, kaolinite, and coal are the most significant components in most dusts from coal mines.

Ten samples of bulk dust collected from coal mines in New South Wales and Western Australia were provided by Pickford and Rhyder Consulting Pty Ltd, Australia. An X-pert pro MPD X-ray diffraction instrument (Malvern Panalytical, Ltd, Malvern, UK) was used to obtain qualitative scans of these bulk samples to identify specific components within these samples. The instrumental parameters for these qualitative measurements

are provided in [Supplementary Information](#) (available at *Annals of Work Exposures and Health* online). These dusts were categorized into three groups (shown in [Fig. 1](#)) based on the crystalline composition and the magnitude in response (high, medium, or low) of the most significant crystalline components using scatter analysis (Xpert Highscore™, Malvern Panalytical Ltd, Malvern, UK). [Table 1](#) describes the sources of the dusts used for the generation of the prediction samples and their composition. [Table 1](#) reports the significant components, although other reflections were also present in the XRD scans indicating the presence of unidentified trace components. Other notable potential mineral components in dust from Australian coal mines include pyrite ( $\text{Fe}_2\text{S}$ ), calcite ( $\text{CaCO}_3$ ), and dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ).

Only dolomite is expected to potentially be present in a significant quantity (greater than 10%) ([Ward et al., 1999](#)). XRD scans of the coal mine dusts from the UK are shown in [Supplementary Information](#) (available at *Annals of Work Exposures and Health* online).

The procedure for the generation of prediction samples is described in [Stacey et al. \(2021a\)](#), however, no pure quartz or kaolinite powder was added to the bulk dust mixtures. Aerosols were generated in a glass jar and the respirable dust was collected onto a 25-mm diameter PVC filter using a Safety in Mines Personal Dust Sampler (SIMPEDS) operating at a flow rate of 2.2  $\text{l min}^{-1}$  (Casella, Bedford, UK). The flow rate through the respirable sampler was calibrated using a TSI 4100 flow metre (TSI Inc., USA). Two bulk samples from Group 1,



**Figure 1.** XRD scans of dust samples from Australian coal mines grouped into three sets based on their crystalline composition. The symbol Q denotes XRD reflections attributable to quartz, K denotes XRD reflections attributable to kaolinite, and O denotes XRD reflected attributed to orthoclase or 'ordered' microcline Feldspar minerals. Minor trace reflections attributed to muscovite 2M1 are not shown.

**Table 1.** Significant crystalline mineral composition and identification of the mine dusts for samples used in the predictions sets.

Identification	Bulk samples	Number of prediction samples	Significant crystalline composition
Australian Group 1	Bulks 8 and 10	12	Quartz (SiO <sub>2</sub> ), kaolinite (Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub> ), trace—mica (muscovite 2M1, KAl <sub>2</sub> (AlSi <sub>3</sub> )O <sub>10</sub> (OH) <sub>2</sub> )
Australian Group 2	Bulks 1 and 2	9	Quartz (SiO <sub>2</sub> ), minor—kaolinite (Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub> )
Australian Group 3	Bulk 9	6	Quartz (SiO <sub>2</sub> ), minor—kaolinite (Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub> ), feldspar possibly microcline or orthoclase (KAlSi <sub>3</sub> O <sub>8</sub> )
UK Coal 1		10	Graphite (C), minor—quartz (SiO <sub>2</sub> ), kaolinite (Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub> ), illite (K <sub>0.65</sub> Al <sub>2</sub> (Al <sub>0.65</sub> Si <sub>3.35</sub> O <sub>10</sub> )(OH) <sub>2</sub> ), pyrite (Fe <sub>2</sub> S)
UK Coal 2		5	Graphite (C), trace—quartz (SiO <sub>2</sub> ), kaolinite (Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub> ), analcime (NaAlSi <sub>2</sub> O <sub>6</sub> ), dolomite (CaMg(CO <sub>3</sub> ) <sub>2</sub> )
South African Durrans (low quartz)		16 13	Described in <a href="#">Stacey et al. (2021b)</a> Minor—quartz (SiO <sub>2</sub> ) and kaolinite (Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub> )

2 bulk samples from Group 2, and 1 bulk sample from Group 3 (containing the highest response from the feldspar mineral) were used to generate 12, 9, and 6 samples, respectively, of aerosolized respirable dust for collection on filters. A total of 16 prediction samples were obtained from the South African mine dust with added kaolinite and quartz from the previous study ([Stacey et al., 2021b](#)) were included and 15 prediction samples from 2 coal seams from a single mine in Wales, in the UK. An additional set of 13 prediction samples (separate to other low quartz content Durrans samples added to the calibration and validation sets) of Durrans coal dust were also prepared to provide an additional check of the models prediction capabilities with low proportions (1–25%) of quartz A9950 and quartz-free kaolinite (Georgia, USA).

#### Independent target 'assigned' values

The procedures used to determine the target values for quartz, kaolinite, and coal are described in [Stacey et al. \(2021a\)](#) and in [Supplementary Information](#) (available at *Annals of Work Exposures and Health* online). In brief, the target mass values for quartz and kaolinite were obtained using a direct on-aerosol-filter XRD method described in the Health and Safety Executive's (HSE) Method for the Determination of Hazardous Substances (MDHS) 101 ([HSE, 2014](#)). The mass of coal was estimated by subtracting the XRD values for kaolinite and quartz from the value for the mass of respirable dust measured gravimetrically using a balance with a

readability of 1 µg (Mettler-Toledo Ltd, Leicester, UK). Therefore, the target value for coal potentially includes other non-quantified substances in the mine dust.

The XRD measurement was verified, when large proportions of kaolinite (an interference) were present, with an indirect furnace-based method, similar to that described in the National Institute for Occupational Safety and Health (NIOSH) method 7500 ([NIOSH, 2004](#)). Calibrations for the indirect method were prepared using a SIMPEDS to collect amounts of aerosol of the HSE quartz standard A9950 ([Stacey et al., 2009](#)) onto 25-mm diameter PVC filters. The PVC filters were then ashed in a furnace and the residue was recovered and filtered onto 0.45-µm pore size silver filters (SKC Ltd, Blandford, UK). A furnace temperature of 450°C rather than the 600°C specified in NIOSH 7500 was used to provide an opportunity to assess if clays other than kaolinite were present. Kaolinite will dehydroxylate to form an amorphous meta-kaolinite or mullite at this temperature and thus kaolinite is removed from the sample, whereas potential contaminant clays like dickite and illite, with reflections at similar XRD positions as kaolinite, decompose at higher temperatures. The temperature of 450°C successfully removed the coal and reduces the potential for the formation of wollastonite from the presence of any significant calcite.

#### Infrared analysis

A Perkin Elmer Frontier FTIR instrument was used with Quant software (Perkin Elmer UK Ltd, Beaconsfield, UK).

The standard conditions in MDHS 101 were used for FTIR analysis (HSE, 2014). Thirty-two scans were collected from 560 to 1000  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$ . Spectral effects due to external factors (e.g.  $\text{CO}_2$  and  $\text{H}_2\text{O}$ ) were compensated for by running a background scan prior to analysis of each batch of filters. A first-order derivative was used to process each spectrum before applying the PCR computational process using the Quant software.

### The chemometrics process

The chemometrics model determines the spectral features in a scan that correlate best with concentration for the quantification or identification of a component. The process centres spectral data to its mean value and derives a new set of coordinates called eigenvectors from  $x$  and  $y$  ordinates for wavenumber and absorbance. The eigenvectors showing the maximum variance on different samples are those that are more closely associated with each individual component, and are reduced to a limited number of components that have the largest influence on the spectral profile i.e. the principal components.

For PCR, each sample is processed until the best possible correlation is obtained from a regression between the values determined for the principal components (known as scores) from a combination of a number of components in the spectral profile and the mass of analyte.

The process is developed further for PLSR, where not only the above is applied, but the scores that determine the maximum variability of the spectral data are also explained by scores generated from the variability of the combinations of sample constituents and mass of analyte and then both sets of data are correlated to find the maximum covariance. PLSR models can potentially be derived that use fewer principal components than the PCR model, because the concentration of a component can be given a low weighting if the derived scores poorly describe the observed variability in the spectra. This may reduce the variability of results obtained when the models are challenged with dusts from different atmospheres; since there is a lower potential for the spectral components to be affected by interference. However, the commercial software offers the potential for the user to optimize the number of principal components for the PCR model. This was done for quartz and kaolinite using the strategy described in Stacey *et al.* (2021b).

### Estimation of precision and the measurement uncertainty

An assessment of the expanded measurement uncertainty is essential to quantify the reliability of the method for a particular measured value and to assess if the method meets international performance requirements.

To calculate the expanded uncertainty, the analytical method uncertainty is combined with that for the aerosol sampling, which is estimated as 10.1% in ISO 24095 (ISO, 2009). These uncertainty components are combined as the square root of the sum of the squared individual uncertainty values which is then multiplied by a coverage factor of 2 to obtain an expanded uncertainty for the whole measurement process (ISO, 2016).

For each analyte, analytical method uncertainties were calculated by applying an approach to estimate it from the calibration relationship, to the unweighted regression relationships between the predicted and assigned target values (Fig. 2). The equation to find uncertainty of an individual measured value from calibration data is given in equation (1).

$$U(X_{\text{pred}}) = \sqrt{\frac{S^2}{b_i^2} \cdot \left( \frac{1}{1} + \frac{1}{n} + \frac{(X_{\text{pred}} - \bar{X})^2}{(\sum (X_i^2) - (\sum X_i)^2/n)} \right)} \quad (1)$$

where  $U(X_{\text{pred}})$  is the estimated uncertainty on the predicted value of  $X_p$  and where in this case,  $X$  is the target assigned value of the analyte derived using XRD direct on-filter method,  $\bar{X}$  is the mean value of all  $X$  and  $X_i$  are the individual values of  $X$  and 'n' is the number of samples.  $S^2$  is the mean residual difference in the value predicted by the model ( $Y$ ) between the observed ( $Y_{\text{obs}}$ ) and the calculated  $Y(Y_{\text{Cal}}) \sum \frac{(Y_{\text{obs}} - Y_{\text{Cal}})^2}{n-2}$ ,  $b_i$  is the slope of best fit for the linear regression (EURACHEM, 2000). To assess the appropriateness of using an unweighted regression, the standard analytical method uncertainties were plotted with the absolute percentage differences for each individual predicted value. In theory, about 60% of absolute differences should be within the analytical method standard uncertainty. Standard deviations of the percentage difference from the target assigned values were also calculated for each analyte in the prediction sample sets.

### Limits of detection

The limits of detection (LOD) were calculated from the standard error of the intercept and slope coefficient of the regression between the predicted and assigned target values for each analyte.

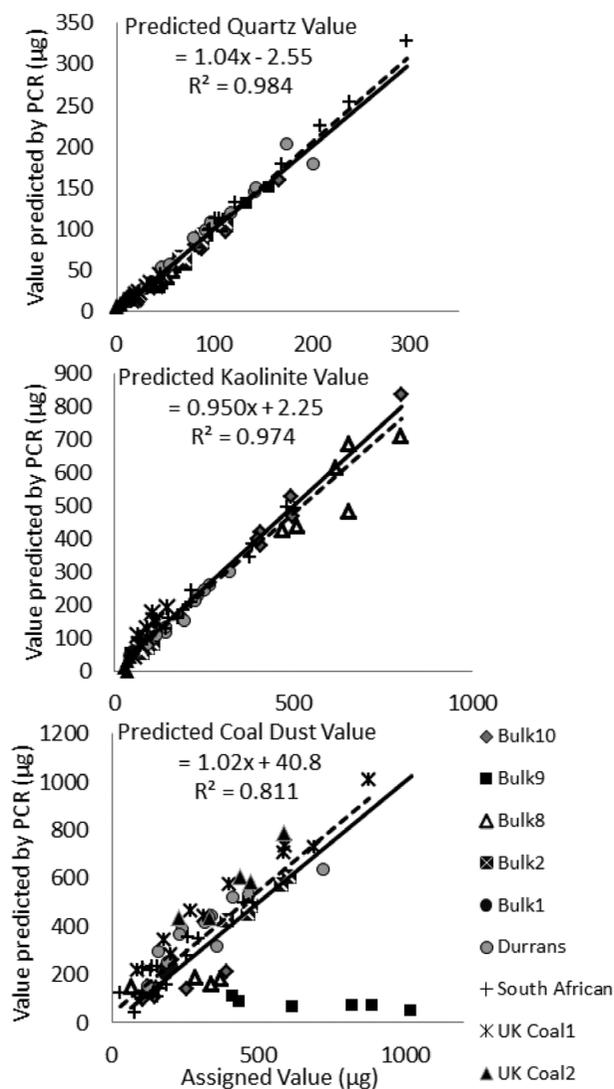
$$\text{LOD} = 3.3 \times (c/b_i) \quad (2)$$

where  $c$  is the standard error of the intercept from the regression and  $b_i$  is the slope of the trend line.

## Results and discussion

### Optimization for the chemometrics models

The measurements of aerosol filter samples sent from Australia (separate to those used for the prediction sets),



**Figure 2.** Predicted values for quartz (top), kaolinite (middle) measured using FTIR with PCR method compared against the assigned target value measured using direct on-aerosol filter XRD analysis and coal dust (bottom) which was compared against the remaining mass of respirable dust (assumed as all coal dust). The straight line drawn on the chart is the ideal 1:1 relationship. The dotted line is the linear trend line for the relationship between the two measurement approaches. The trend line equation for coal dust excludes samples from Bulk 9 with the feldspar mineral.

and evaluated for this study using XRD, identified that most respirable dusts from coal mines contained less than 20% quartz whilst some samples had more than 50% kaolinite. These values were outside the range of most calibration and validation samples prepared for the previous PCR or PLSR models (Stacey *et al.*, 2021a). The proportion of kaolinite in some of the Australian aerosol filter samples was more than that found in some British mines (up to 40%) in the 1970s (Dodgson and Whitaker, 1973).

The following changes were introduced to optimize the models for Australian coal mine dusts. Firstly, an additional 13 samples, of artificial mixtures of Durran's coal dust, kaolinite, and 1–10% of HSE quartz standard A9950, were added to the calibration and validation sets. Secondly, the XRD calibration range for quartz was investigated and reduced from 1000 to 400  $\mu\text{g}$  to reduce the influence of a few calibration points with higher loadings when measuring low quartz values. New

calibration coefficients were derived for quartz and new target values were assigned to each calibration and validation sample. The spectrum range for processing was reduced to from 1000 to 966  $\text{cm}^{-1}$  to improve the consistency of predicted values for kaolinite.

The average proportions of quartz, kaolinite, and coal in the prediction samples containing dust from Australian coal mines were 11.5% (range 4.9–23%), 37% (range 4.8–84%), and 51% (8.5–89%), respectively. The average proportions in the prediction samples containing dust from UK mines were 4.2% (range 3.5–5.8%), 15.9% (range 11.7–24.6%), and 80% (range 69.6–84.6%) in UK Coal 1 and 0.7% (range 0–1.1%), 4.5% (range 0–8.6%), and 94.8% (range 90.5–100%) in UK Coal 2 for quartz, kaolinite, and coal, respectively. Durrans coal dust contained artificially mixed proportions of quartz (3–33%) and kaolinite (21–39%). A list of proportions for each prediction sample is shown in [Supplementary Information](#) (available at *Annals of Work Exposures and Health* online).

### The PCR model

Figures comparing the values calculated by the PCR for the calibration and validation samples with their assigned target values are provided in [Supplementary Information](#) (available at *Annals of Work Exposures and Health* online) as [Fig. S3](#) for quartz, [Fig. S4](#) for kaolinite, and [Fig. S5](#) for coal. Statistics from the software recalculation of the PCR model are shown in [Table 2](#).

[Fig. 2](#) compares the predicted values obtained from the PCR model with the target values for quartz, kaolinite, and coal.

### Verification of the assigned target values

Assigned target values for quartz were checked on 10 filters using XRD and a separate indirect recovery XRD method when the proportion of kaolinite in the sample was high (above 50%); since significant interference could occur for the principal and secondary quartz reflections at 2 theta degrees of 26.6 and 20.9. The average difference and standard deviation from the PCR predicted values from the target values were  $-10.4 \pm 6.2\%$ , and the difference from the indirect XRD analysis

method involving the furnace recovery process was  $-7.7 \pm 6.6\%$ . The means are not significantly different with a *t*-test probability (*P*) value for equal variance of 0.38, which is more than 0.05.

### Precision, limit of detection, and uncertainty

For the PCR model, the average percent difference from the assigned target value was 0.78,  $-1.57$ , and 13.4% for quartz, kaolinite, and coal, respectively, with standard deviations of 15.4, 17.5, and 63.8%. While for the PLSR model, for the purposes of the comparison, the average percent difference from the assigned target value was 4.03, 0.02, and 65.1% for quartz, kaolinite, and coal, respectively, with standard deviations of 15.8, 18.8, and 60.2%.

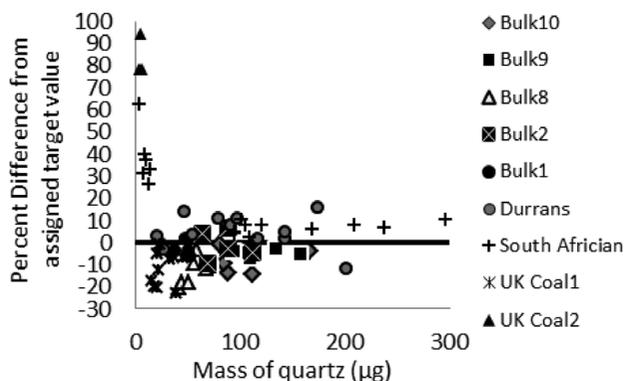
The percentage difference from each assigned target value for quartz, showing the spread and bias of individual results, is in [Fig. 3](#).

Values for the LODs were 5.0  $\mu\text{g}$  (quartz), 25  $\mu\text{g}$  (kaolinite), and 71  $\mu\text{g}$  (coal) for the PCR and 4.7  $\mu\text{g}$  (quartz), 29  $\mu\text{g}$  (kaolinite), and 96  $\mu\text{g}$  (coal) for the PLSR method, respectively. None of the values for coal include results from Bulk 9. The values for quartz are close to the LOD and limit of quantification of 3 and 10  $\mu\text{g}$ , respectively, for the FTIR method reported in MDHS 101 (HSE, 2014). The approach used to calculate the LOD for XRD in the MDHS 101 method is different from the chemometrics approach applied to FTIR because it is determined by making repeat measurements on clean filters. An LOD of 5  $\mu\text{g}$  corresponds to a quartz concentration of 10  $\mu\text{g m}^{-3}$ , assuming a 4-h sample collected at a flow rate of 2.2  $\text{l min}^{-1}$ .

The estimated standard uncertainty of these measurements (which should be equivalent to about 1 SD of values) from the PCR model for quartz, kaolinite, and coal are plotted in [Fig. 4](#) together with the absolute percentage difference of the individual results from the assigned target values. About 60–70% of the absolute percent difference values are below the standard uncertainty trend line for each analyte (quartz, 61%, kaolinite, 70%, and coal, 62%). Ideally, the estimate should represent 60% results; so 70% is a slightly cautious estimation of the analytical method uncertainty for kaolinite

**Table 2.** Statistics for the PCR models for quartz, kaolinite, and coal in artificial mixtures of Durrans coal dust.

Analyte	Number of principal components	Percent of explained variance (%)	Standard error of the regression ( $\mu\text{g}$ )	Standard error of the predictions ( $\mu\text{g}$ )
Quartz	3	99.5	9.1	9.6
Kaolinite	2	96.9	25	25
Coal	18	99.7	15	32



**Figure 3.** Precision of the FTIR and PCR method when measuring quartz in coal dust samples from various sources with three principal components.

measurements. A small number of extreme values were excluded from the calculation of the standard uncertainty relationships where the residual difference for the predicted value was greater than a  $z$  score of 3 (quartz = 2, kaolinite = 3, and coal = 1).

Uncertainties were higher for kaolinite and coal than for quartz (Fig. 4). For coal, the variability was due to differences between the sources of the mine dusts (Fig. 2), the relatively few prominent distinguishing features in its spectra (Stacey *et al.*, 2021a), and the uncertainty of the gravimetric measurements themselves.

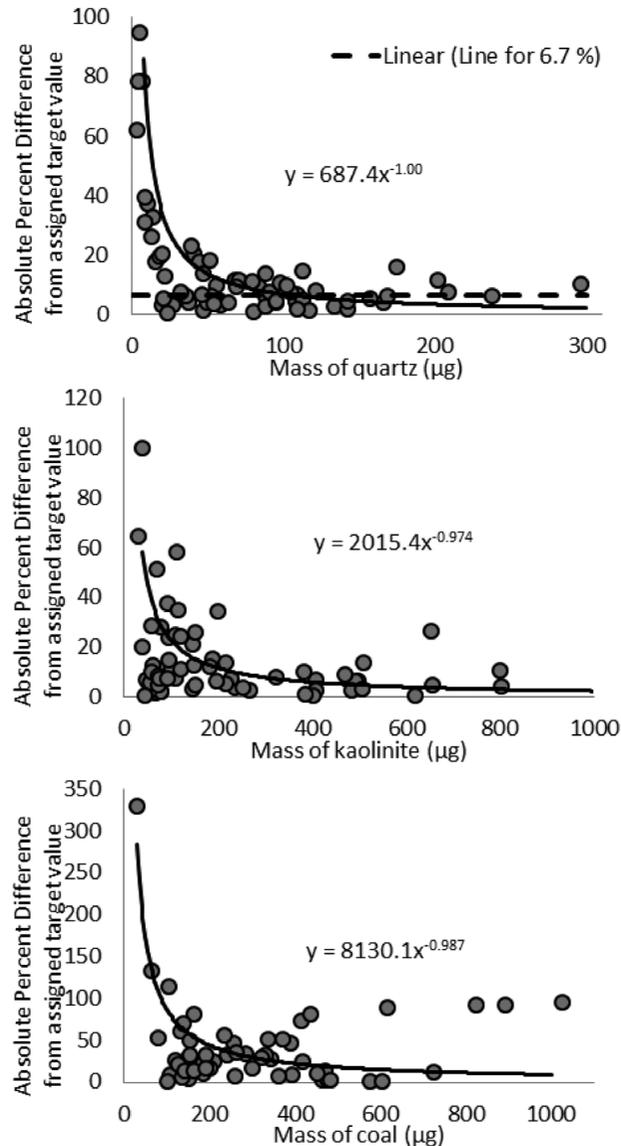
The chemometric models for coal are calibrated with a coal dust that is relatively free of other components, whilst real samples also contain minor or trace levels of other substances (Table 1, Fig. 1, and Supplementary Fig. S1, available at *Annals of Work Exposures and Health* online) included in the gravimetric analysis, besides quartz and kaolinite. This may introduce some additional uncertainty for the assigned value for coal. In addition, a principal component value of 18 for coal is relatively high and may result in over modelling, which may poorly predict samples that are independent from the calibration and validation. However, smaller numbers of principle components increased the differences between the predicted and assigned values for coals from different bulk samples. A typical example is demonstrated for the results obtained using the PLSR model with seven principal components (Supplementary Fig. S8, available at *Annals of Work Exposures and Health* online). The larger number of principal components potentially compensates for any spectral differences attributable to a specific characteristic of the coal in the mine dust e.g. the higher crystallinity coals from the UK.

For kaolinite, the low XRD intensity for the principal reflections, relative to quartz, influenced the uncertainty precision for the target values; however, higher relative

errors were also obtained for some mass values above 500  $\mu\text{g}$  (Fig. 2, Bulk 8). Samples with amounts of illite (such as the UK coal samples) reported consistently higher results for kaolinite. The PLSR model was affected to a greater extent (Supplementary Fig. S7, available at *Annals of Work Exposures and Health* online). This difference is potentially due to similar O–H absorbance near those for kaolinite at 915  $\text{cm}^{-1}$ , the presence of poorly crystalline clays, or interference from dolomite; which has an absorbance close to that for kaolinite at 900  $\text{cm}^{-1}$ .

The values of uncertainty for quartz are of particular interest because of its health concern and its relatively low occupational WEL, namely 0.1  $\text{mg m}^{-3}$  (100  $\mu\text{g m}^{-3}$ ) in GB and 0.05  $\text{mg m}^{-3}$  (50  $\mu\text{g m}^{-3}$ ) in Australia. The trend line equation for quartz (Fig. 4) indicates that the analytical uncertainty is about 6.7% (1 SD) when measuring a mass of 103  $\mu\text{g}$  collected from an aerosol containing 100  $\mu\text{g m}^{-3}$  of quartz, using a standard respirable sampler operating at 2.2  $\text{l min}^{-1}$  for a full 8-h working shift. The standard uncertainty for the analytical method increases to 13% when the sampling time is reduced to 4 h. This is also the uncertainty if measuring half the mass, namely a mass of 53  $\mu\text{g}$  of quartz from an aerosol containing 50  $\mu\text{g m}^{-3}$  of quartz using a standard respirable sampler operating at 2.2  $\text{l min}^{-1}$  for a full 8-h working shift.

A value of 33% was obtained for the expanded uncertainty at 53  $\mu\text{g}$  (representative of an aerosol of 50  $\mu\text{g m}^{-3}$ ). This expanded uncertainty value is close to the  $\pm 30\%$  performance requirement specified in the international standard ISO 20581 for measuring occupation exposure limits (ISO, 2016). Measurements will meet the ISO 20581 expanded uncertainty requirement for measurement at the GB WEL if the sample is collected for about 4 h 30 min with existing equipment or a higher

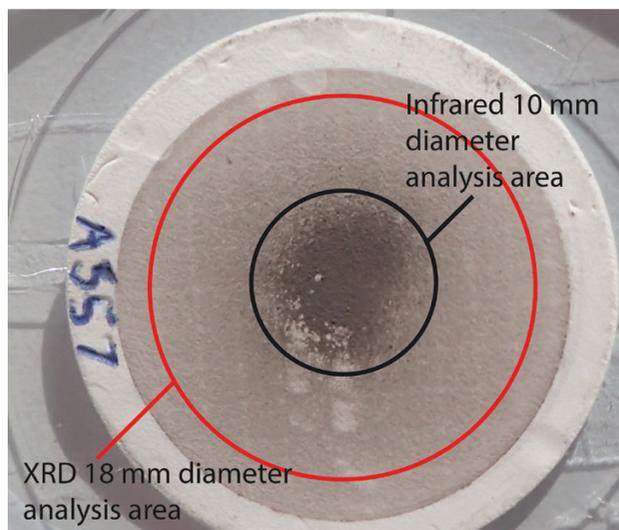


**Figure 4.** Calculated uncertainties for quartz, kaolinite, and coal dust predictions using the FTIR and PCR method. The trend line is the analytical method uncertainty calculated using the formula for determining analytical uncertainty from calibration data. The dots represent the absolute relative difference for individual results from the assigned target value.

flow rate sampler is used at about  $4 \text{ l min}^{-1}$  to sample more than 528 l of the workplace atmosphere. Different respirable samplers may also have different deposition profiles for the collected aerosol (ISO, 2015). If a higher flow rate sampler is used with this PCR model, it will be necessary to check that the sensitivity is the same as that obtained from the SIMPEDS; which was used to prepare the calibration and validation standards.

The WEL for respirable kaolin in GB is higher than that for RCS at  $2 \text{ mg m}^{-3}$  (i.e.  $2000 \text{ } \mu\text{g m}^{-3}$ ) (HSE,

2005b) where the predicted analytical precision would be about 1.2%. In this case, the uncertainty would be purely limited by the variability of the sampling apparatus. Internationally, exposure limits for respirable dust in coal mines vary from about  $400$  to  $3000 \text{ } \mu\text{g m}^{-3}$  (IFA, 2021). GB has deemed respirable dust, when present at a concentration in air equal to, or greater than,  $4 \text{ mg m}^{-3}$  ( $4000 \text{ } \mu\text{g m}^{-3}$ ) as a time-weighted average over an 8-h period, to be a substance hazardous to health and so the Control of Substances Hazardous to Health (COSHH)



**Figure 5.** A filter containing respirable coal dust with some dust lost from the filter's centre. A circle with a diameter of approximately 18 mm in diameter is drawn on the filter to represent the estimated analysis area for the XRD measurement and a similar circle of approximately 10 mm in diameter is drawn for the FTIR analysis area.

regulations apply (HSE, 2005a). Most exposure standards for respirable dust in coal mines are based on measuring the total respirable dust captured using gravimetric analysis. A PCR measurement might not be appropriate to assess exposure to a respirable coal mine dust standard since it employs a different metric to more specifically quantify the coal, and results for the respirable fraction would be lower than that reported in historical data. The specific PCR measurement does, however, provide hygienists, other occupational health professionals, regulators, and duty holders with better detailed information about the nature of the exposure, i.e. the proportions of major constituents (e.g. quartz and kaolinite present in the coal dust).

### Practical issues

In a limited number of samples (Fig. 4), the comparability between XRD target values and FTIR results was compromised due to the potential for loss of dust from the centre of the aerosol filters containing coal mine dust (Fig. 5) at mass loadings around or greater than 0.5 mg. Losses occurred during transport from the sampling location to the laboratory, when removing the filter from its cassette for analysis, transfer to and from a filter holder for the FTIR and prolonged exposure in the infrared beam. Fig. 5 shows the typical image for loss of coal mine dust from the centre of an aerosol filter. The clear patches towards the centre are areas where the dust has fallen off. This is a particular problem for FTIR analysis since the analysis area for these instruments is

typically 6–10 mm. The FTIR results will be lower than the XRD value because the XRD is able to analyse a wider area (about 18 mm in diameter) and so the loss of dust is proportionally less.

Filter handling and transport is an important part of the analytical process for samples containing coal; since dust can be lost from the filter's centre, which is the within the area measured by the FTIR instrument. Filter cassettes designed to minimize handling may have an important role in reducing the potential for dust loss. It would be advantageous to measure the samples as close to the worksite as possible to reduce the potential for losses of dust during transport. Portable FTIR instruments are one option that would facilitate the analysis of samples at the site by hygienists or duty holders. Calibrations between these portable FTIR instruments were shown to be comparable (Ashley *et al.*, 2020) which implies that a single chemometric method may also be transferable between instruments.

### Conclusion

The PCR model accurately measured quartz and kaolinite in dusts from a range of coal mines, from different countries and Australian states, containing a variety of different minerals, coal types, and proportions of these minerals in their matrix.

The expanded uncertainty of measurements for quartz, kaolinite, and coal when using the FTIR and PCR method either met or were close to the international

performance requirements for occupational exposure measurements at airborne concentrations equivalent to current GB and Australian WEL.

For quartz, the expanded measurement uncertainty meets the requirements of ISO 20581 at the GB WEL concentration of  $0.1 \text{ mg m}^{-3}$  ( $100 \text{ } \mu\text{g m}^{-3}$ ) when sampling for 4.5 h using a respirable sampler operating at  $2.2 \text{ l min}^{-1}$ . An 8-h sampling period would be needed when measuring an RCS aerosol at the Australian WES concentration of  $0.05 \text{ mg m}^{-3}$  ( $50 \text{ } \mu\text{g m}^{-3}$ ), which would be suitable when monitoring mine workers since sampling generally occurs for their whole working shift (often about 8–12 h).

The LOD for quartz of  $5.0 \text{ } \mu\text{g}$  is comparable with those published for direct on-aerosol filter measurement methods like that for XRD in MDHS 101, where the limit of detection is determined by analysis of clean unused filters and the calibration relationship is by the measurement of a pure quartz standard. A limit of detection of  $5.0 \text{ } \mu\text{g}$  equates to a quartz concentration of  $10 \text{ } \mu\text{g m}^{-3}$ , (which is 1/10th of the current GB exposure limit of  $0.1 \text{ mg m}^{-3}$ ) assuming a 4-h sample collected at a flow rate of  $2.2 \text{ l min}^{-1}$ .

## Supplementary Data

Supplementary data are available at *Annals of Work Exposures and Health* online.

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## Disclaimer

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## Data availability

Data will be shared on reasonable request to the corresponding author.

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