
Original Article

Comparison of the Analysis of Respirable Crystalline Silica in Workplace Air by Direct-on-Filter Methods using X-ray Diffraction and Fourier Transform Infrared Spectroscopy

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Abstract

A comparison of the analysis of respirable crystalline silica direct-on-filter methods using X-ray diffraction (XRD) and Fourier transform infrared (FT-IR) spectroscopy was undertaken using 253 real workplace air samples from road construction and tunnelling, coal mining, and kitchen benchtop manufacturing in Australia. Using pure α -quartz standards, XRD and FT-IR direct-on-filter analyses produced identical test results, however, the real workplace samples showed a clear discrepancy between FT-IR and XRD results with on average a 9% positive bias of the FT-IR results. The cause of the positive bias was due to matrix interferences which was confirmed by using synthetic mixture air samples. Approximately a third of the data by direct-on-filter method using FT-IR was assessed to be invalid based on the peak height ratio criterion due to excessive interferences and weight overload limitations. The XRD method showed better results due to less interference from the common matrices. XRD could handle up to twice the sample loading and at higher loadings up to 7 mg when a correction was applied. It was also able to achieve a lower limit of detection of 2 $\mu\text{g filter}^{-1}$ when a slower scan condition was utilized.

Keywords: α -quartz; direct-on-filter method; FT-IR; RCS; respirable crystalline silica; respirable dust; silica exposure; X-ray diffraction

Introduction

Internationally, respirable crystalline silica (RCS) occupational exposure limits (OELs) are being reassessed and

in some jurisdictions lowered, putting pressure on the capabilities of the analytical techniques used to achieve robust analyses and reliable detection limits. The current time-weighted average (TWA) OEL in Australia, Austria,

What's Important About This Paper

This study compares direct-on-filter X-ray diffraction (XRD) and Fourier transform infrared (FT-IR) spectroscopy detection of α -quartz using air samples from major industries in Australia. Importantly, this study found FT-IR results had a 9% bias relative to XRD results caused by matrix interference. The XRD method experienced less interference from common matrices, including at higher loading. Accurate, sensitive quantitation of respirable crystalline silica is necessary to assess compliance with occupational exposure limits and health risks.

Estonia, Finland, Germany, Spain, and the USA is 0.050 mg m^{-3} , compared with 0.03 mg m^{-3} in Japan, and 0.025 mg m^{-3} in Portugal; and the American Conference of Governmental Industrial Hygienists also recommends 0.025 mg m^{-3} (OSHA, 2016; ACGIH, 2019; JSOH, 2020; Safe Work Australia, 2020; The European Network on Silica, 2020). To adequately monitor compliance to these lower limits of RCS with the current sampling techniques, a reduction of the limits of detection (LODs) for the analytical methods is required.

Currently, most laboratories participating in the LGC UK international interlaboratory proficiency scheme and proficiency analytical testing (PAT) in the USA use Fourier transform infrared (FT-IR) or X-ray diffraction (XRD) as analytical techniques for analysis of RCS (Stacey *et al.*, 2003; Harper *et al.*, 2014). The techniques used are divided into five methods of direct-on-filter and indirect techniques, each with different characteristics and limitations (NIOSH, 1994, 2003, 2017; HSE, 2015; ISO, 2015, 2018).

The direct-on-filter method has very little preparation other than presenting the filter to the instrument on the required filter mount. This is a significant advantage as it eliminates any losses compared with more complicated preparation procedures. This simple method also reduces analysis time and variability of the test results between laboratories. Few comparison studies of direct-on-filter methods for the determination of RCS in relation to matrix interferences and LODs have so far not been adequately conducted (Stacey *et al.*, 2003; Kauffer *et al.*, 2005).

A comparison is presented here between the two most commonly used methods, 'direct on filter using XRD' and 'direct on filter using FT-IR' utilizing real workplace airborne dust samples collected from Australian industry sectors such as road construction and tunnelling, coal mining, and kitchen benchtop manufacturing. The encountered interferences from the sample matrix and the LODs in each method are discussed.

Methodology

Pure α -quartz air standards

Pure α -quartz calibration standards were made from the respirable fraction of pure α -quartz certified reference

materials (CRMs) National Institute of Standards and Technology NIST SRM 1878a ($93.7 \pm 0.21\%$, NIST, 2005), and Sikron F600-A9950 Health and Safety Laboratory UK ($96.3 \pm 1.4\%$, Chisholm, 2005), deposited onto a 25 mm polyvinyl chloride (PVC) filter (GLA 5000, Pall Corporation) from a dust generator through a plastic cyclone sampler (SKC) under the same flowrate condition (2.2 l min^{-1}) as real workplace samples following the Australian Standard AS 2985 (Standard Australia, 2009) methodology.

The amount of α -quartz deposited on the filter was measured gravimetrically using a 6-digital Mettler Toledo XP6 microbalance with a readability of $1 \mu\text{g}$ in accordance with the Australian Standard AS 2985 (Standard Australia, 2009). The filters were equilibrated to the room atmosphere overnight ($18 \pm 2^\circ\text{C}$; RH: $64 \pm 13\%$) and any static charge was eliminated before the measurements were performed. To correct the effect of the temperature and humidity differences between pre-sampling and post-sampling, two blank filters were measured with the samples, and the difference of the average blank values was used for the gravimetric correction.

Additional samples from the LGC UK interlaboratory proficiency program and its predecessor the Workplace Analysis Scheme for Proficiency conducted by the Health and Safety Laboratory UK (WASP HSL) were also used as pure α -quartz calibration standards with the consensus value found in the proficiency round being used as the amount on the filter. The calibration line was compiled from the NIST SRM 1878a, the Sikron F600 CRMs and the proficiency program samples.

Workplace air samples

Real workplace air samples ($n = 253$) were assembled from a cross section of different worksites and industries. These were collected from 34 different sampling sites in Australia from 2014 to 2018, covering major Australian industries including road construction and tunnelling (47%), coal mining (23%), kitchen benchtop manufacturing (25%), and others (5%). The samples were collected through a plastic respirable cyclone sampler at a flowrate of 2.2 l min^{-1} . The pump calibration

and other sampling procedures were in accordance with the standards (ISO, 2009; Standard Australia, 2009).

The detected matrices in the real workplace respirable dust samples were generally a mixture of several materials. The matrices differed between the sampling sites, even when collected within the same industry sector. From within the same sampling sites, the matrices were similar. All samples showed varying percentages of α -quartz in the respirable dust.

Synthetic mixture air samples

To investigate the effect of the interference, synthetic air samples were prepared by mixing of pure α -quartz with a variety of other pure materials. Three materials, cristobalite (NIST CRM1879a), kaolinite (Ajax Chemicals Pty Ltd), and iron oxide (Fe_2O_3 , Merck & Co. Inc.) were selected since they were detected as common matrices in the workplace samples.

The synthetic samples were prepared in two steps. At first, approximately 0.1 mg of pure α -quartz was deposited onto a filter by a plastic cyclone sampler following the same procedure as the standard air samples above and weighted. Then, one of the matrices was deposited onto the filter by the same procedure and reweighed. The total dust loadings for all samples were less than 1 mg. The matrix concentration against the total dust was calculated with these gravimetric results. The range of the matrix concentration was aimed to have a comparable range to the workplace samples. Any effect of the layering of the materials was considered to be negligible as the dust loadings were less than 1 mg (ISO, 2015; Skoog *et al.*, 2017).

Statistical data analysis

All statistical calculations in this paper were conducted using Microsoft Excel 2013 (Version: 15.0.5153.1000) from first principles. The FT-IR/XRD method comparison of the real workplace samples was performed using the Student's paired *t*-test following the Bland–Altman approach on the logarithm of the square of the difference of the methods compared with the average (Bland and Altman, 1999; Giavarina, 2015).

Analytical techniques

Direct-on-filter using XRD

XRD measurements were performed using a Panalytical X'Pert Pro XRD with a X'celerator detector and a Cu-target X-ray tube. The sample filter was loaded horizontally onto a sample holder which spins, but remains horizontal during the X-ray measurement, so that

almost the total deposition area (21 mm diameter) was analysed to give a more complete analysis. A silver filter was placed underneath the sample filter to be used for sample overload correction if needed. The X-ray beam power was 45 kV and 40 mA. The scan speed was 0.84 $2\theta/\text{min}$.

The peak intensity of the α -quartz (101), (100), and (112) crystalline lines was used to determine the amount of α -quartz and to additionally examine the presence of interference from the matrix. If the ratio of evaluated results from (101) line and the average of the three lines was outside the range 0.9–1.1, then initially the sample diffractogram was examined more carefully, and subsequently the second (100) or third (112) lines were used when the main (101) line had unacceptable interference (National Health and Medical Research Council, 1984; HSE, 2015; ISO, 2015). When the dust loading was more than 2 mg, the overload correction was employed by using the peak intensity of Ag (111) and (200) crystalline lines (Atree-Williams *et al.*, 1977).

Direct-on-filter using FT-IR

FT-IR measurements were performed using a Perkin Elmer Spectrum Two FT-IR. It was used at a resolution of 4 cm^{-1} and with an infrared beam diameter of approximately 8 mm at 800 cm^{-1} . The spectra obtained were the result of 32 scans which were averaged to reduce the signal noise. The sample filter was fixed onto a sample holder and placed vertically in the instrument. In this study, the samples were analysed by XRD first, then analysed by FT-IR as the samples when presented in the FT-IR had to be tilted vertically.

A PVC filter has large absorption peaks around 800 cm^{-1} and as such the thickness and/or pore density of the filter will determine the extent of this interference. Furthermore, most filters will vary in thickness and/or pore density across the diameter of the filter. Hence, an infrared spectrum pre-scan of the filter is necessary to obtain a background spectrum that can be subtracted from the sample spectrum. This blank correction is best performed using the actual sample filter. However, this is not always possible. In this study, 20 blank filters with different weights were pre-scanned. Then, a blank correction was performed using a pre-scanned spectrum of a blank filter of a similar weight. The average difference between the blank filter weights of the samples and the blank filters for the correction was $0.045 \pm 0.037\text{ mg}$. It should be noted that the simple subtraction includes an inherent error due to the multiplicative nature of the transmission errors from the sample and filter layers combined.

The absorbance of infrared energy from Si–O vibrations at 800 and 780 cm^{-1} was used to measure the

α -quartz and to examine the interference from the matrix. The peak height ratio at 800 and 780 cm^{-1} was calculated. If this ratio was outside the range 1.0–1.4, the sample spectrum was examined carefully and the discrepancy was usually confirmed to be due to interference on the α -quartz peaks, rendering the data as invalid and was subsequently excluded. Also, for a valid analysis the dust loading needed to be less than 1 mg filter^{-1} (HSE, 2015; ISO, 2018).

The interference corrections for kaolinite by using the absorbance ratio between 800 and 915 cm^{-1} and for cristobalite by using the absorbance ratio between 800 and 620 cm^{-1} , were applied to the workplace and synthetic mixture samples when the spectrum showed the kaolinite or cristobalite presence (Pickard *et al.*, 1985; NIOSH, 2003, 2017; Lee *et al.*, 2013; HSE, 2015). In this study, these standardized correction methods were applied to the FT-IR results and compared before and after the correction. Several interference correction methods for multiple matrices have been studied (Miller *et al.*, 2017; Salehi *et al.*, 2021), however, they require similar matrices in the samples to be used in the calibration standards. Moreover, they require the matrices to be known beforehand. The procedures are not simple to use particularly for the samples from various workplaces with unknown matrices.

Results

Calibration lines and estimation of the LOD

The α -quartz calibration lines for direct-on-filter using XRD and FT-IR are shown in Fig. 1. Pure α -quartz CRM standards were used. The calibration lines for XRD and

FT-IR showed good linearity with $r^2 = 0.998$ when the amount was between 0 and 2 mg filter^{-1} and $r^2 = 0.996$ between 0 and 1 mg filter^{-1} , respectively. The XRD continued to show good linearity up to 7 mg filter^{-1} of pure α -quartz CRM with $r^2 = 0.998$ when the overload correction was applied for samples above 2 mg filter^{-1} (data points not shown in graph).

An increasing standard deviation can be seen with increasing amounts of α -quartz by XRD and FT-IR methods in Fig. 2. Each level was evaluated by measuring three different filters loaded with approximately equal amounts of a pure α -quartz standard. The filters were measured in triplicate to establish an estimate of the standard deviation at that level. The standard deviation of the XRD and FT-IR analyses was similar in magnitude. The LOD was estimated by extrapolating the found standard deviation regression relationship to zero α -quartz and then multiplying the standard deviation y intercept by 3. It was found that the estimated LODs based on this approach using pure α -quartz were 10 $\mu\text{g filter}^{-1}$ for both XRD and FT-IR direct-on-filter methods. The detection limit of α -quartz using XRD depends largely on the instrumental conditions. The estimated LOD of 10 $\mu\text{g filter}^{-1}$ was determined at the scan speed of 0.84 $2\theta/\text{min}$ for the α -quartz (101) line. This estimated LOD and signal noise could be reduced by increasing the scan time. The corresponding LODs of 5, 2.4, and 1.9 $\mu\text{g filter}^{-1}$ were achieved by using slower scan speeds to 0.25, 0.084, and 0.051 $2\theta/\text{min}$, respectively.

The correlation between pure α -quartz standard amounts on a filter ($n = 43$) measured by XRD and

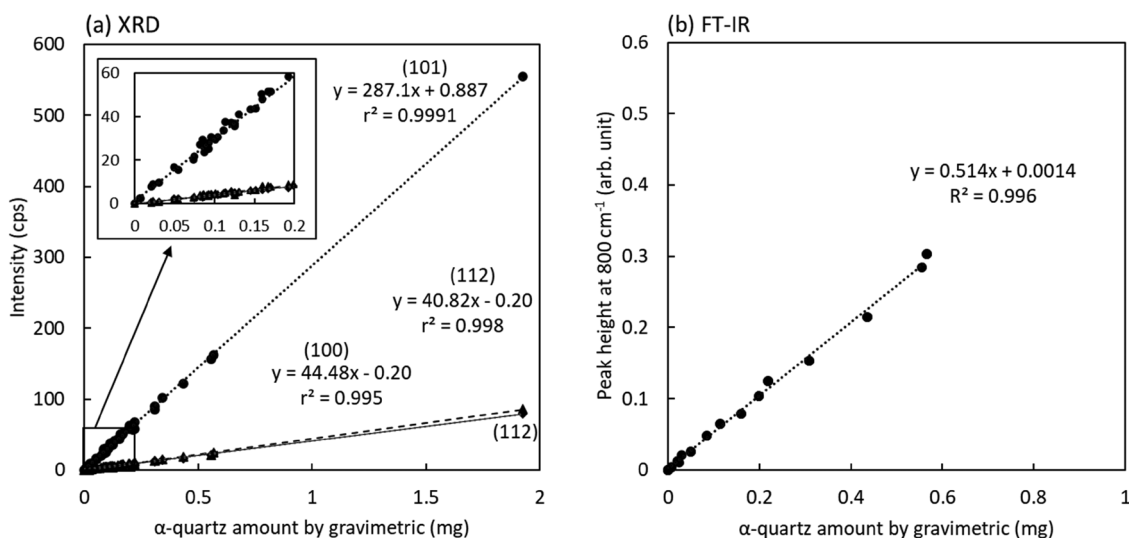


Figure 1. Calibration lines for α -quartz by (a) XRD showing the response of the 101 (dots), 100 (dashes), and 112 (solid) lines and (b) FT-IR absorbance response at 800 cm^{-1} .

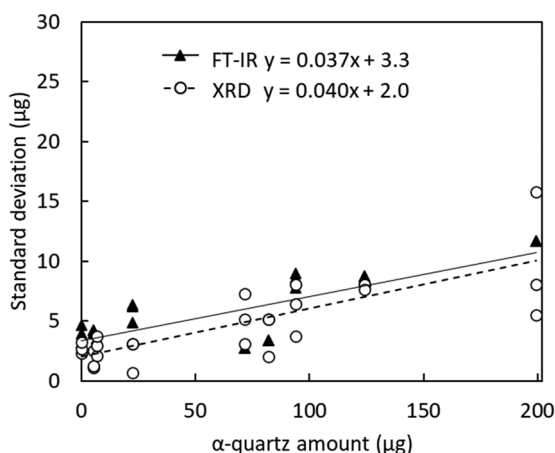


Figure 2. The standard deviations of the α -quartz analysis by XRD and FT-IR.

FT-IR can be seen in Fig. 3. This shows good agreement with a coefficient of determination of $r^2 = 0.992$ and correlation parameters of slope 1.01 ($P = 0.378$) and intercept 0.005 mg ($P = 0.142$) indicating that the slope is not significantly different from 1.0 and the intercept is not significantly different from zero.

Quantification of α -quartz in real workplace samples

The number of the workplace samples with the percentage of α -quartz in the loadings with less than 20% was 89, with between 20 and 40% was 59, with 40 and 60% was 51, with 60 and 80% was 38, and with higher than 80% was 16.

The relationship between the amount of α -quartz in real workplace matrix samples ($n = 253$) measured with XRD and FT-IR can be seen in Fig. 4. The FT-IR data were assessed for validity by using the peak ratio quality assurance criterion by calculating the peak height ratio at 800 and 780 cm^{-1} . The data were assessed to be invalid if the ratio returned a value outside the range of 1.0–1.4 indicating matrix interference was observed in the spectra. Furthermore, for FT-IR to be a valid analysis the total dust loading on the filter should also be less than 1 mg in weight (HSE, 2015; ISO, 2018).

The number of data points that were assessed to be invalid was 82, which was 32% of the total 253 samples analysed. The data were classified as invalid when the dust loading was greater than 1 mg ($n = 33$), or outside the peak height ratio of 1–1.4 ($n = 26$), or failed both criteria ($n = 23$).

The percentage of invalid data increased dramatically as the matrix concentration increased. The invalid data in the samples with less than 60% matrix were 23%

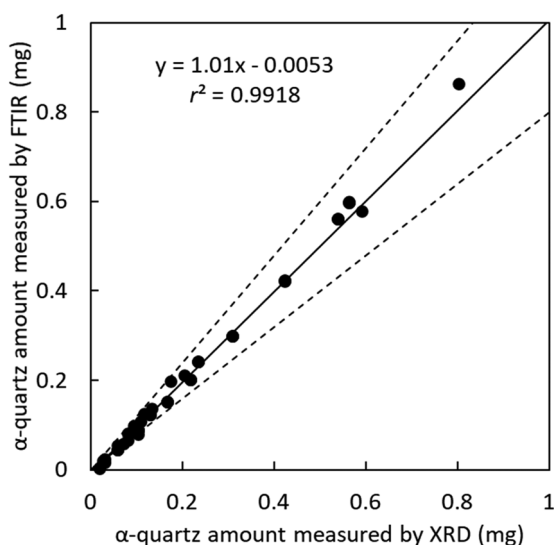


Figure 3. The relationship between α -quartz amounts in pure α -quartz samples measured by XRD and FT-IR ($n = 46$). The dashed lines show $\pm 20\%$ of unity slope.

($n = 24/105$). The invalid percentage increased to 32% in the samples with 60–80% matrix ($n = 19/59$) and 44% with more than 80% matrix ($n = 39/89$).

Of all the samples ($n = 253$) studied, only a single sample showed interference in XRD analysis in the (101) line ($<0.5\%$ of the total samples) and no samples showed interferences on all three lines.

Fig. 4a shows the valid data before kaolinite/cristobalite correction. The valid data ($n = 171$) show a correlation between XRD and FT-IR analytical results with a coefficient of determination of $r^2 = 0.971$. The correlation slope of 1.10 shows that the FT-IR test results had on average a 10% positive bias in comparison to the XRD results.

Fig. 4b shows the data with kaolinite/cristobalite correction. The coefficient of determination became $r^2 = 0.972$ and the correlation slope became 1.09. The change was slight, and the FT-IR test results had on average a 9% positive bias in comparison to the XRD results. A Student's paired t -test following the Bland–Altman approach found that the XRD and FT-IR test results were significantly different from each other ($P < 0.05$).

In this study, acceptance limits of $\pm 20\%$ between the methods were adopted (HSE, 2015) and shown as dotted lines in Fig. 4. A proportion of 29% of the valid samples ($n = 49/171$) showed more than $\pm 20\%$ differences between FT-IR and XRD values. The proportion changed to 27% ($n = 47/171$) when applied the matrix correction. Regression analysis gave a $P < 0.05$ in comparison

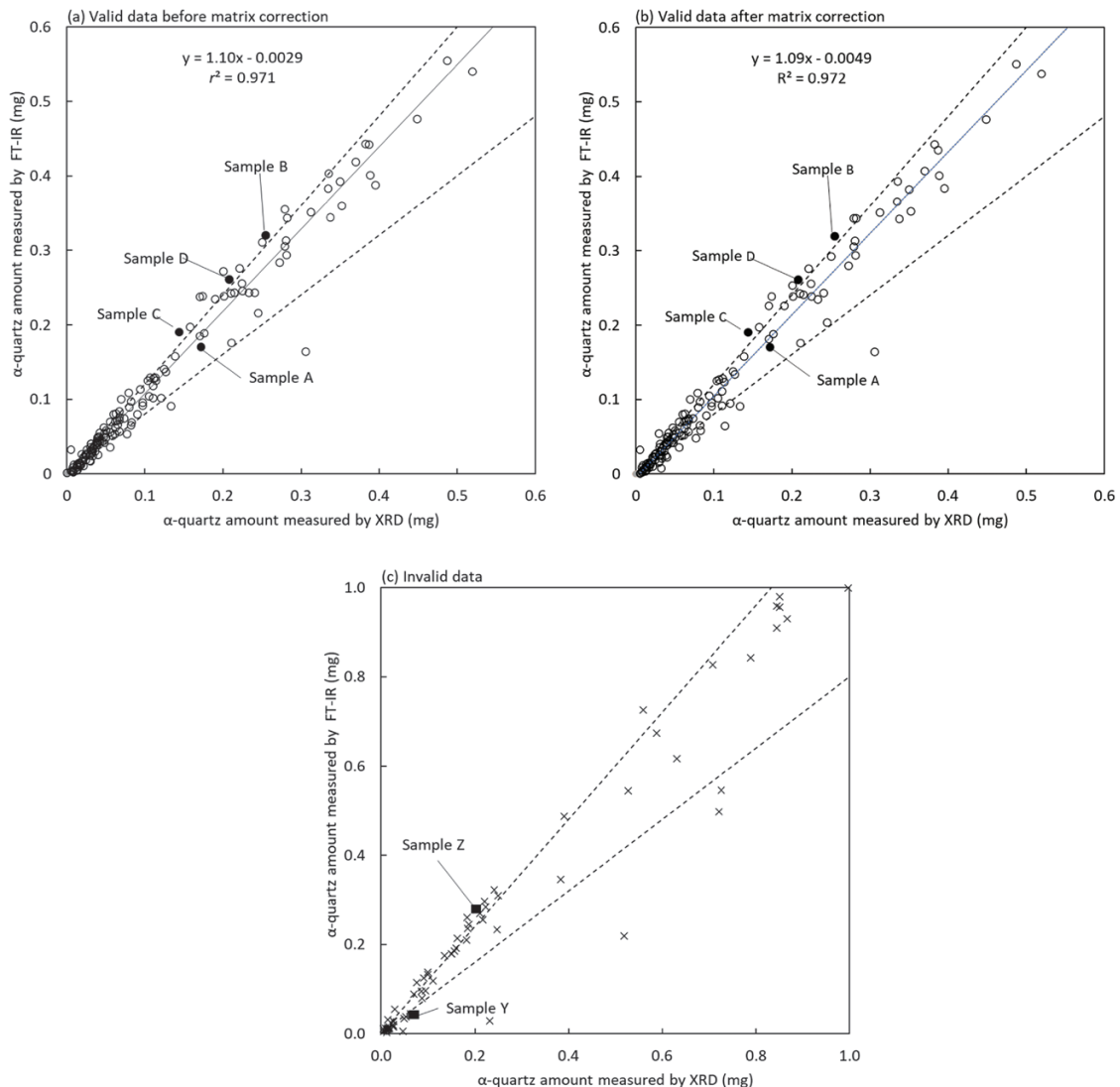


Figure 4. The relationship between α -quartz amounts in real workplace matrix samples measured with XRD and FT-IR ($n = 253$). The circles show valid data ($n = 171$) before (a) and after matrix correction (b), and cross marks show invalid data (c) ($n = 82$). The closed marks show the samples used for data analysis in Fig. 5. The dotted lines are $\pm 20\%$ from unity slope.

to a unity regression slope. As the previous comparison of the pure α -quartz samples in Fig. 3 showed no bias with a slope close to unity, the comparison of the real workplace samples tends to indicate reduced equivalence due to sample matrix effects in the FT-IR analyses.

Data analysis of real workplace matrix samples

To investigate the cause of the discrepancies between the analyses results, the XRD and FT-IR spectra of typical samples A, B, C, D, Y, and Z were reviewed (see Fig. 4). The major matrices detected by XRD analysis are kaolinite ($n = 164$, including samples B, Y, Z), calcite

($n = 122$, including samples B, C, Y, Z), albite ($n = 22$, including samples C, Z), and cristobalite ($n = 10$, including sample D). Some samples ($n = 127$) showed small interferences that could not be identified as the peaks were too small and/or were overlapped with other components.

XRD analysis showed 72% of samples with two or more than two interfering matrices ($n = 182/253$, including samples B, C, Y, Z), 14% ($n = 35/253$, including samples D) with one interfering matrix, and 14% ($n = 36/253$, including sample A) without any interfering matrixes.

Fig. 5a,b show the XRD diffractogram and FT-IR spectra for sample A, respectively. The measured amounts of α -quartz were 0.172 for XRD and 0.170 mg for FT-IR with a total respirable dust amount of 0.21 mg on the filter. This is an average percentage of α -quartz to dust of 82%. The α -quartz (101), (100), and (112) lines were all observed in the XRD diffractogram and the α -quartz peaks at 800 and 780 cm^{-1} were observed in the FT-IR spectrum. No significant matrix interference was observed in either XRD or FT-IR spectra. The peak height ratio at 800 and 780 cm^{-1} in FT-IR was 1.2, which is within the valid range of 1.0–1.4.

Fig. 5c,d and e,f are the spectra for the samples B and C, respectively, which show a positive 20% higher test results in FT-IR. Kaolinite peaks were observed in the both XRD and FT-IR spectra of sample B and albite peaks were observed in the spectra of sample C. There is no interference from kaolinite and albite in the XRD spectra, however peak overlaps were observed in the FT-IR spectra. The peak height FT-IR ratio for samples B and C was 1.4 and 1.0, respectively, which are within the limits of the valid analysis range. As a result, the α -quartz amount by FT-IR was 0.320 mg filter^{-1} while that by XRD was 0.255 mg filter^{-1} in sample B, and for sample C the α -quartz amount by FT-IR was reported as 0.190 mg filter^{-1} while that by XRD was 0.144 mg filter^{-1} . The FT-IR results showed a 26 and 32% higher test results than the XRD values. The concentration of α -quartz in sample B was 36% of 0.71 mg of total respirable dust and 16% of 0.89 mg of total respirable dust in sample C. In comparison to sample A, the positive bias observed in samples B and C can be considered due to a higher percentage of matrix material containing interferences. When applied the kaolinite correction to the FT-IR data for sample B, the test result corrected to 0.310 mg, which was 22% higher than the XRD result.

Fig. 5g,h are the spectra for sample D from the kitchen benchtop industry, showing cristobalite peaks in both the XRD and FT-IR spectra. There is no interference from cristobalite in the XRD diffractogram, however peak overlap was observed in the FT-IR spectrum such as other silicate cases above. As a result, the α -quartz amount by FT-IR was 0.261 mg filter^{-1} while that by XRD was 0.208 mg filter^{-1} in sample D. The FT-IR results showed a 26% higher test values than the XRD values. The peak height FT-IR ratio for sample D was 1.2, which is within the limits, and the data were plotted as a valid result in Fig. 4. The concentrations of α -quartz and matrix in sample D were 59 and 41% of 0.35 mg of total respirable dust. The cristobalite amount by XRD was 0.037 mg filter^{-1} and the ratio to total respirable dust was 11%. When applied the cristobalite

correction to the FT-IR data for sample D, the result corrected to 0.252, which was 21% higher than the XRD result.

In Fig. 5i–l, the spectra for samples Y and Z are presented. Strong calcite peaks were observed both in the XRD and FT-IR spectra for sample Y. Calcite and several silicates peaks were observed in the spectra of the sample Z. Iron oxide peaks and the increase of the background were only observed in the XRD spectrum of the sample Z. There was no interference from the matrix in the XRD diffractogram, however peak overlaps were observed in the FT-IR spectra. The FT-IR peak shapes were distorted, and the peak height ratios were 1.7 and 1.6, which were well outside of the valid range. The loaded dusts in samples Y and Z were 4.51 and 1.97 mg, which are beyond the 1 mg measurable limit by FT-IR. The α -quartz amounts by FT-IR in samples Y and Z were 0.044 and 0.278 mg filter^{-1} , however, the analysis was rejected due to the criteria of the peak height ratio and the high dust loadings. The α -quartz amounts by XRD in samples Y and Z were 0.063 and 0.203 mg filter^{-1} and the concentrations of α -quartz in the dust were 1.4 and 10%. Thus, the concentration of the matrix in the dust was 98.6 and 90%, which is considerably higher than other samples, though the proportion of the matrix that causes the interference is unknown.

It is well known that the presence of iron in samples increases the background signal in XRD spectra when using a Cu-X-ray tube (Cullity, 1978; Mos *et al.*, 2018). The amount of iron in the samples was determined by XRF analysis when iron oxide peaks or an increase in the background was observed in XRD diagram. The iron oxide found in the workplace dust samples was determined to be less than 20% in all samples in this study.

Qualitative interference from various matrices

To verify the interference effect from the matrix, three synthetic mixture samples comprising α -quartz and one of three materials, kaolinite, cristobalite, or iron oxide, were examined. The recovery ratios of approximately 0.1 mg α -quartz in the dust matrices are compared in Fig. 6. In the graphs, the closed mark shows valid results. If the unacceptable interference was present, based on the criteria for the methods, the data were plotted with an open mark.

The recovery of approximately 0.1 mg α -quartz in the synthetic mixture samples of α -quartz and kaolinite is shown in Fig. 6a. The FT-IR results showed positive bias when the sample comprises more than approximately 50% of kaolinite while the XRD results remained within the $\pm 20\%$ tolerance. After the kaolinite correction was applied to the FT-IR results the recovery

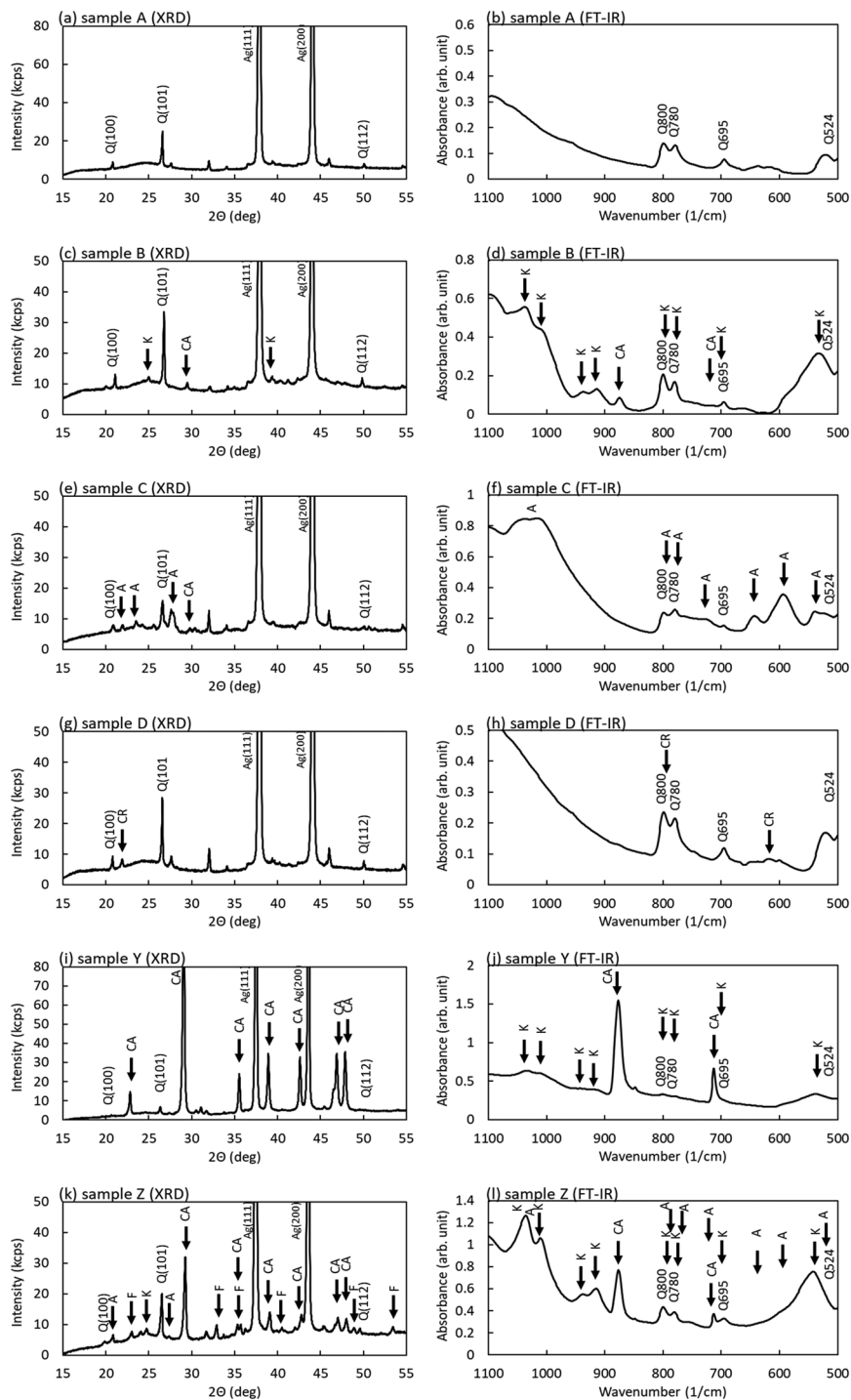


Figure 5. The XRD and FT-IR spectra of typical samples A (a, b), B (c, d), C (e, f), D (g, h), Y (i, j), and Z (k, l). The letters 'Q', 'K', 'A', 'CA', 'CR', and 'F' in the spectra show the peaks related to α -quartz, kaolinite, albite, calcite, cristobalite, and iron oxide, respectively.

became closer to 1, however the recovery exceeded the 20% tolerance when approximately >70% kaolinite was present in the sample.

The recovery of approximately 0.1 mg α -quartz in the synthetic mixture samples of α -quartz and cristobalite is shown in Fig. 6b. The FT-IR results showed

a positive bias when the sample comprised only approximately 15% of cristobalite while the XRD results remained within the $\pm 20\%$ tolerance up to 95% of cristobalite. In the cristobalite mixture, the positive bias for FT-IR was observed at a significantly lower matrix ratio than in the kaolinite mixture. When applied the cristobalite correction, the FT-IR results recovery became closer to 1, however the recovery exceeded the 20% tolerance at more than 40% cristobalite.

Fig. 6c shows the recovery of approximately 0.1 mg α -quartz in the synthetic mixtures of α -quartz and iron oxide. The recovery for the iron oxide mixtures by FT-IR remained within the $\pm 20\%$ tolerance up to 90% iron oxide. The recovery by XRD showed a negative bias when the sample comprised approximately $>90\%$ of iron oxide, which is likely to be due to the increase of background signal by the fluorescence of iron.

Discussion

Possibility of a lower LOD

International OELs for crystalline silica are being reduced due to the increasing awareness of the risk of health effects occurring at lower exposure levels. This trend calls for a lower analytical LOD. An LOD of

$10 \mu\text{g filter}^{-1}$ will not be sufficient to adequately test for compliance to a lower OEL. (Stacey, 2007). If an OEL of 0.025 mg m^{-3} is implemented, an LOD of preferably less than $2.5 \mu\text{g filter}^{-1}$ is required to confirm compliance within an 8 h TWA sample.

Clearly, as the LOD is dependent on the precision of an analysis, any factor that contributes to the variability will increase the standard deviation and hence the LOD. In FT-IR, the main influencing factor to determine the LOD is the error of blank correction as the PVC filter in FT-IR analysis has an absorbance at 800 and 780 cm^{-1} . The error is due to differences between blank filters and/or the differences between measured points on the filter. Furthermore, the absorption of the dust sample also contributes to the error when the blank subtraction is conducted by the simple subtraction without consideration of the multiplicative nature of the transmission. These errors can be minimized if the blank subtraction is calculated accurately based on Maxwell's equations as infrared is an electromagnetic wave, however, this may not be practicable due to the considerably complex calculation.

The estimation of the LOD by the determination of the standard deviation of the analysis of a blank PVC filter was stated in some methods (HSE, 2015; ISO,

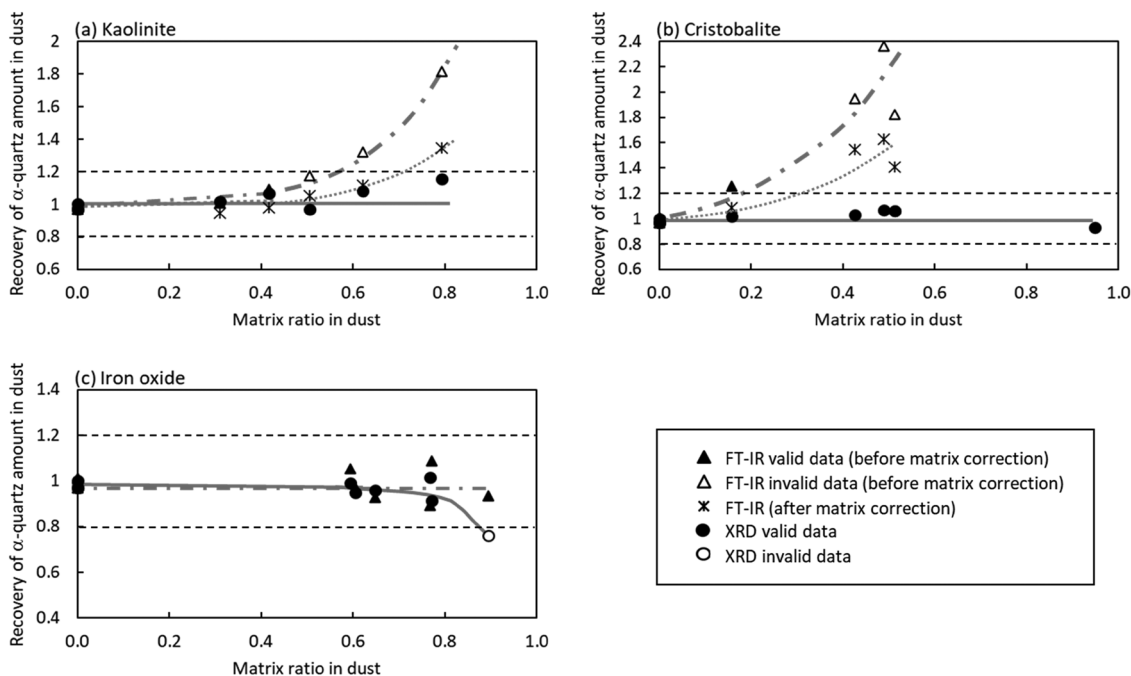


Figure 6. The recovery of α -quartz amount (approximately 0.1 mg) by XRD and FT-IR for the 3 synthetic mixture samples, kaolinite (a), cristobalite (b), and iron oxide (c). The x-axis shows the amount of matrix to dust as a ratio. The closed marks show valid results and the open marks show invalid results based on the criteria for the methods. The stars show the FT-IR results with matrix correction. The dashed lines show $\pm 20\%$ of the 100% recovery, which define the borderlines for the valid analysis.

2018). To estimate the LOD for a method, the number of blank samples and analytical procedure should be selected carefully. If only one blank filter was measured 10 times, and thus the results were collected with the same blank spectrum, the resulting LOD might be optimistic (ISO, 2018). This is because the signal-to-noise ratio (SNR) of FT-IR signal is high and the contribution of the signal noise to the standard deviation is negligible. The absorbance difference between filters and the blank correction errors by absorbance of dusts contribute significantly more to the LOD than the signal noise. A more accurate method of determining the LOD by FT-IR would be to determine the standard deviation from repeated measurements of a small amount of α -quartz in a dust sample loaded onto a filter, acknowledging also that very low amounts of material on a filter is very difficult to accurately produce. The standard deviation of a filter analysed that is loaded with a matrix material of interest alone may give a better estimate of the LOD.

Conversely, the main influencing factor to determine the LOD in the analysis by XRD is the instrumental SNR of the measured diffractogram. Interference from the PVC filter is negligible as the α -quartz peak is quite strong compared with the PVC signal. The SNR can be improved by using a slower scan rate. A four times slower scan rate can provide a two times better SNR. The scan speed of 0.84 2θ /min for the α -quartz (101) line was used to estimate the LOD of 10 $\mu\text{g filter}^{-1}$. When the condition was changed to a slower rate, the XRD achieved an LOD of 2 $\mu\text{g filter}^{-1}$. This means that XRD can be adapted to a lower OEL when needed.

Interference from matrices

The interference from silicates is a major issue in the analysis of α -quartz by FT-IR. This is because the peaks around 800 cm^{-1} are associated with Si-O bond vibration, which is observed in all silicates. In direct-on-filter FT-IR analysis approximately 50% kaolinite or 15% cristobalite in the dust showed a greater than 20% positive bias in the α -quartz test results of the synthetic mixture in Fig. 6. When kaolinite/cristobalite correction was applied, the α -quartz recovery improved, however, it still showed at approximately 60% of kaolinite or 30% of cristobalite in the dust a greater than 20% positive α -quartz bias.

A study by Lee *et al.* (2013) showed a positive 20% α -quartz bias when more than 90% kaolinite and more than 0.4 mg dust loading was analysed by FT-IR. Our results confirmed that the kaolinite correction only functions in limited concentration range and does not function well at higher matrix concentrations and higher dust loadings.

Analysis by FT-IR of the workplace samples showed the difficulty of the correction with other matrices. For example, in Fig. 6a, the positive bias of the FT-IR test result without correction in the 62% kaolinite synthetic sample gave a result of 1.32 as the recovery of α -quartz, however, when a correction was applied this reduced to 1.11, which is a more acceptable result. The FT-IR test result for sample B which contained less than 64% kaolinite and calcite was 0.320 mg. With the correction this reduced to 0.310 mg showing 22% positive bias. This discrepancy was caused by the presence of calcite in the sample B. The baseline for the kaolinite peak at 915 cm^{-1} for the correction was tilted due to the overlapped calcite peak at 875 cm^{-1} . The absorbance of the kaolinite peak was therefore estimated smaller than the actual absorbance. When several peaks are detected at close wavenumbers, adjacent peaks can often affect the analysed peak and should be carefully assessed by the analyst to obtain valid results.

Albite also contributed a positive bias to the α -quartz test result. For example, the sample C showed 32% positive bias of the FT-IR test result compared with the XRD result. The FT-IR spectra in Fig. 5f showed the strong albite peaks and the distorted α -quartz peaks.

The interference from calcite is slightly different from silicates since the calcite has strong absorption at 875 and 712 cm^{-1} , which does not overlap with the α -quartz peaks directly. However, the wider tail from 875 to 712 cm^{-1} does overlap with α -quartz absorption peaks at 800 and 780 cm^{-1} (Reig *et al.*, 2002). This signal tail results in a tilted baseline of sample Y which in turn causes a negative bias on the FT-IR α -quartz result.

Conversely, there was little or no interference observed from the matrix in XRD analyses. This is due to the peak intensities of α -quartz being relatively stronger than most other silicates such as kaolinite and albite (ICDD, 2020). The combinations of d -spaces, which results in 2θ angles are different from α -quartz and hence can be analysed without difficulty. In cases where the main (101) line has unacceptable interference then the second (100) or third (112) line can be used. Therefore, the XRD is the more robust technique to analyse α -quartz accurately in real samples.

It is shown that iron oxide acts as a negative interference in the analysis of α -quartz by XRD due to the increase of background signal. However, for this interference to significantly affect the analysis it needs to be in a concentration greater than 90% in the dust. The analysis of iron by XRF in all the dust samples was found to be less than 20% and could therefore not have caused any negative bias in the samples analysed in this study. It should be noted that the interference from iron

oxide generally does not affect the ratio of obtained results from the three lines. To obtain valid results, it is important to check any interference from the matrix not only to analyse the α -quartz lines but also to analyse the full scan diffractogram.

This study shows that the commonly found silicates in workplace samples can cause a positive bias in FT-IR analyses. These interferences can be found by diligent inspection of the FT-IR spectrum and revealed by anomalous peak height ratios rendering the results invalid. The discrepancies between FT-IR and XRD results in the real workplace samples are attributed to the positive bias given by the matrix interferences in the FT-IR spectrum.

Considerations when interpreting FT-IR results

For samples Y and Z, the peak height ratio and dust loading criteria were used to check for the presence of any interference in the samples and enabled the elimination of invalid FT-IR test results. These criteria showed that 32% of the workplace FT-IR test results were deemed invalid and subsequently removed. This illustrates the limitations of the direct-on-filter analysis with the FT-IR technique.

Samples B, C, and D showed a more than 20% bias resulting from interferences from silicates such as kaolinite, albite, and cristobalite, however, the peak height ratio criteria did not detect such interferences. A 27% proportion of the valid FT-IR test results of the workplace samples showed more than a 20% bias compared with the XRD results.

In most cases, the peak ratio criterion detected the kaolinite interference when the FT-IR test results showed positive bias in Fig. 6a. However, sample B showed a positive bias due to other matrices but was assessed by the peak ratio criterion to be valid. Multiple matrix interferences are complicated and difficult to detect in FT-IR spectra. Furthermore, the correction may not be functional when multiple matrices and/or high matrix concentrations are detected as discussed earlier in *Interference from matrices*.

Therefore, to obtain valid analytical results, it is essential to check for interference from the matrix by using not only the peak ratio criterion but also to diligently inspect the FT-IR spectra for any additional anomalies and to carefully understand these limitations.

Conclusion

The two direct-on-filter methods using XRD and FT-IR were compared by using real workplace air samples. When using pure α -quartz standards, identical results are found with XRD and FT-IR. However, evaluation of

253 real workplace samples from different Australian industries showed an average discrepancy of 9% between FT-IR and XRD results due to matrix interferences. Typically, a positive bias of the FT-IR results was found to be caused by the interference of silicates absorbing around the 800 cm^{-1} wavenumber. To obtain valid FT-IR results, it is critical to evaluate the spectrum for matrix interferences and consider the peak height ratio and sample loadings.

Compared with FT-IR, it was found that XRD was a significantly more robust technique to analyse real workplace samples due to less interferences from the common matrixes, with the exception of high iron loaded samples. XRD could handle up to twice the sample loading and even higher loadings to 7 mg when a correction was applied. Moreover, by selecting a slow scan speed XRD analysis could achieve a lower LOD down to 2 $\mu\text{g filter}^{-1}$ for the instrument used.

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Conflict of interest

The authors declare no conflicts of interest relating to the material presented in this article.

Data availability

The data underlying this article cannot be shared publicly due to confidential nature. The reasonable request will be considered.

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