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Feasibility of the quantification of respirable crystalline silica by mass on aerosol sampling filters using Raman microscopy

Peter Stacey,^{a*} Kerstin T. Mader^b and Christopher Sammon^b

Airborne respirable crystalline silica (RCS) is a hazard that can affect the health of workers, and more sensitive measurements are needed for the assessment of worker exposure. To assess the use of Raman microscopy for the analysis of RCS particulate collected on filters, aliquots of quartz or cristobalite suspended in isopropanol were pipetted onto silver filters. Samples were measured by arbitrarily selecting positions along the filter and collecting spectra at 50 discrete points. The calculated limits of quantification on test samples were between 0.066–0.161 and 0.106–0.218 μg for quartz and cristobalite, respectively. Three respirable quartz calibration dusts (A9950, NIST 1878 and Quin 1B) with different mass median aerodynamic particle sizes obtained similar Raman response relationships per unit mass. The difference between NIST 1878 and Quin 1B was not significant ($p = 0.22$). The intermediate measurement precision of replicate samples was 10–25% over the measured range for quartz (0.25–10 μg) and could potentially be improved. Results from mixtures of quartz and cristobalite were mostly within 10% of their theoretical values. Results from samples of 6% quartz in calcite were close to the theoretical quartz mass. The upper measurement limit for a mixture of 20% RCS in the light absorbing mineral hematite (Fe_2O_3) was 5 μg . These data show that Raman spectroscopy is a viable option for the quantification of the mass of respirable crystalline silica on filters with a limit of detection approaching 1/10th of that obtained with other techniques. The improvement in sensitivity may enable the measurement of particulate in samples from low concentration environments (e.g. inside a mask) or from miniature samplers operating at low flow rates. ©2017 Crown copyright. *Journal of Raman Spectroscopy* published by John Wiley & Sons, Ltd.

Keywords: respirable crystalline silica; workplace; Raman; limit of detection; quantification; particle size

Introduction

Respirable sized particles can penetrate to the alveoli of the lung.^[1] Their aerodynamic size range is defined by an International Organisation for Standardisation/Centre European de Normalisation/American Congress of Government Occupational Hygienists convention^[1] as those particles mostly $<16 \mu\text{m}$ with a 50% penetration cut-off value of 4 μm . Inhalation of respirable particles from an aerosol containing crystalline silica is linked to diseases such as silicosis^[2] and cancer.^[3] In 2004, an estimated 907 cases of cancer in Great Britain were attributed to exposure from aerosols containing respirable crystalline silica (RCS) in the workplace.^[4] RCS is also thought to cause of chronic obstructive pulmonary disease.^[5] Quartz and cristobalite are two crystalline polymorphs of silica that are encountered in aerosols in the workplace. Quartz is a common component in many naturally occurring mineral products, whilst cristobalite is often present in industrial processes where a silica-containing material is heated to around 1000 °C. There is a requirement under the Great Britain's Control of Substances Hazardous to Health regulations^[6] to control exposure to below the current WEL for RCS of 100 $\mu\text{g m}^{-3}$, as a time weighted average for an 8 h working shift.

X-ray diffraction (XRD) and infrared spectroscopy (IR) are two techniques specified by national analytical methods to measure RCS in dust collected on an air sample filter.^[7] Limits of detection (LOD) for XRD and IR reported for RCS measurements on laboratory test samples of pure analyte are between 3 and 10 μg .^[7] Aerosol samplers that typically operate at 2 l min^{-1} are not able to collect

sufficient sample for a quantifiable mass of RCS (20–30 μg) in less than 2 h^[7,8] when sampling an RCS concentration around the WEL. This level of analytical performance limits the capabilities of sampling to evaluate the protection and exposure of workers, e.g. to enable analysis of short-term or task-specific samples within the working shift or from some low concentration environments. Although airborne concentrations of RCS are generally low, there are industrial processes that may expose workers to high concentrations above the WEL, and the use of face filtering masks as respiratory protective equipment (RPE) is frequently employed to protect workers. The exposure of a worker wearing a mask is estimated by applying a correction factor to the results obtained from a personal sample taken outside of the mask. If the RPE is functioning as intended, the expected airborne concentration of RCS inside the mask will be between 0.2 and 1 times the LOD of current

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analytical techniques for a typical 960-l pumped air sample when collected at 2 l min^{-1} during an 8 h working day. A goal of this work was to investigate the use of alternative measurement techniques, with better LOD, to measure the very low airborne concentrations of RCS inside a mask. Ultimately, the aim is to find a technique sensitive enough to permit the analysis of samples to assess the workplace effectiveness of RPE.

Raman spectroscopy is sensitive to both chemical and morphological changes within a sample and is routinely used to distinguish between polymorphs, including those of microcrystalline silica.^[9] This technique was used to quantitatively analyse opaline in silica nodules of volcanic origin utilising a rotating stage to obtain an average signal from the sample surface and produce calibration curves by mass for quartz, cristobalite, coesite and calcite mixtures.^[10] Raman spectroscopy was also investigated as a potential technique to determine the mineral content of rocks on moons or planets.^[11] Only recently has Raman spectroscopy been used to characterise airborne particles of dust from samplers collecting particulate matter $<10 \mu\text{m}$ and particulate matter $<2.5 \mu\text{m}$ from ambient air.^[12–14] Potgieter-Vermaak and Van Grieken^[12] examined the suitability of a number of filter materials for the evaluation of individual aerosol particles using micro-Raman spectroscopy. Catelani *et al.* determined the percentage of particles in samples of airborne dust from two sites using a point count method.^[13] Quartz compositions by number ranged from 4.5% to 12%. The chemical composition of marine aerosols over the Pacific Ocean was also recently examined with an aluminium foil on a 'streaker' sampler being used as a collection substrate for an on-air-sample filter analysis approach.^[14] The work reported in this article investigates the use of a wide area coverage approach to quantification, where the Raman spectra of crystalline silica from many different fields of view are combined.^[15] The advantage of a wide-field measurement approach is that it reduces the variability of the analysis caused by the inhomogeneity of the sample deposit, which is a major factor affecting the reliability of Raman quantification.^[15]

Experimental

Reagents and test sample preparation

Suspensions of the NIST reference material 1878a for quartz and 1879 for cristobalite ($10 \mu\text{g ml}^{-1}$) were prepared in isopropanol (CAS 67-63-5). These suspensions were constantly agitated with a magnetic stirrer. Aliquots (0.1–2 ml) of these suspensions were deposited onto 25-mm diameter, 0.45- μm pore size silver filters (SKC Ltd., Bedford, UK). The deposit area was constrained to a 5-mm diameter area using a bespoke fluted filter funnel. A 5-mm diameter hole in a 25-mm diameter plastic washer was fitted beneath the filter to reduce the sintered suction area and the spread of the sample. Figure S1 shows the filtration equipment, mask and a sample of hematite dust on the deposit area of a silver

filter. The circumference of the deposit area was marked with a needle, before deposition. The scratched circumference clearly demarcated the deposit area from the blank filter in reflected white light under the microscope.

To assess if the Raman measurement is also affected by particle size differences, we compared two other quartz calibration powders with different mass median aerodynamic particle size distributions. The origin of the materials and differences in median aerodynamic particle size^[16] are listed in Table 1.

Raman measurement strategy

Raman spectra were collected from the 5-mm diameter deposit area using an In-Via Raman microscope (Renishaw Ltd., Gloucester, UK) with near infrared laser (785 nm) excitation, CCD camera and a grating with 1200 l mm^{-1} . Typical spectra for quartz and cristobalite standards on silver filters are shown in Fig. 1.

The sample deposit was located on a silver filter, and 50 fields of view were randomly selected from within the 5-mm diameter of the scratched circumference. Raman spectra were obtained from within each field of view using an $\times 20$ objective. The analysis area was estimated as $100 \mu\text{m}^2$, so approximately, 20% of the deposit area would be analysed from 50 sampling points. The spectrum for each sampling point was collected with 100% laser power with a 7-s exposure time and three accumulations. The integrated areas of the Raman peaks were obtained by fitting with a Gaussian line shape using the standard algorithms in the manufacturer's WiRE 4 software package. The areas under the peaks at 462 cm^{-1} for quartz and 410 cm^{-1} for cristobalite were quantified if they appeared within the spectra from each sampling point. The trend between accumulated area counts and theoretical mass was plotted for both polymorphs of crystalline silica.

The signal from a silicon wafer (Si) standard was measured using the integrated area at 520 cm^{-1} with an $\times 50$ objective at 10% laser power for 1 s once before and after each filter analysis. The results of these measurements were used as an external standard to compensate for fluctuations in laser intensity. Daily fluctuations in laser intensity were corrected using the ratio between the count collected when the silicon area was first measured and the average collected before and after each filter measurement.

Statistical evaluation

The difference in trend lines for the measured response and mass relationships between calibration dusts were determined using a *t* statistic calculated from the difference between the slopes of the lines and their standard errors.

An estimate of the intermediate precision was made by analysing five replicate mass loadings of quartz on silver filters at five different measurement levels, incorporating analyses conducted on different days by different researchers to account for any additional variability from the analysts.

Table 1. Origin and median aerodynamic sizes of respirable quartz calibration dusts tested to assess the influence of particle size on Raman response

Name	Origin	Aerodynamic size (μm)		Crystallinity percent
		Mass median	Number median	
NIST 1878a	National Institute for Science and Technology (United States of America)	3.72	1.52	93.7 ± 0.21
A9950	The Health and Safety Executive (Great Britain)	6.04	1.39	89.3 ± 1.86
Quin 1 Bulk	Institut National de Recherche et de Sécurité (France)	7.16	3.24	95.2 ± 2.51

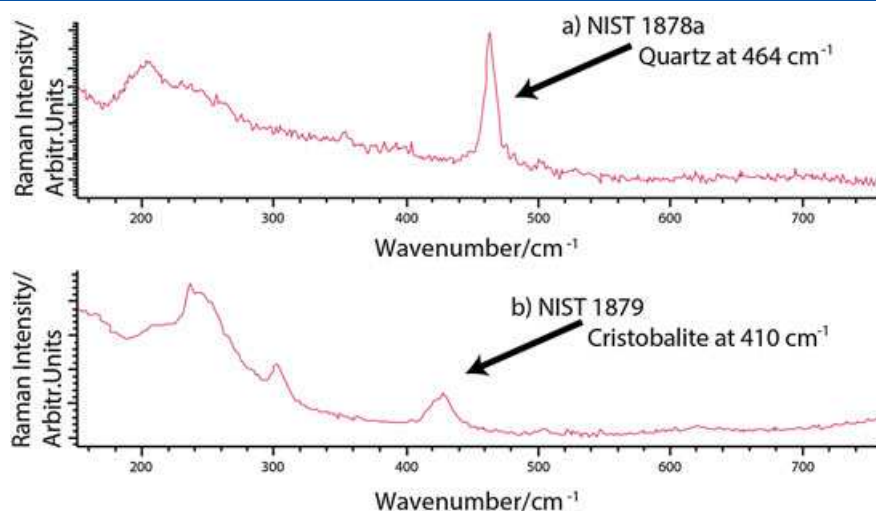


Figure 1. Spectra for quartz and cristobalite collected from a single field of view from a filter-containing 10 µg of analyte deposited in a 5-mm diameter area. [Colour figure can be viewed at wileyonlinelibrary.com]

Precision and bias of pipetting

Test samples, with mass loadings greater than 2 µg, were first measured using an XRD X-pert Pro MPD instrument (Panalytical Ltd., Cambridge, UK) with focusing Bragg–Brento geometry to provide a correction for pipetting errors. The silicon content of some of the highest loadings of reference material on silver filters was measured using inductively coupled plasma atomic emission spectroscopy (Perkin Elmer, Beaconsfield UK). The mass of quartz calculated from the silicon content measurement was used to assess bias in the pipetting. The LOD of this technique was calculated to be approximately 3 µg.

Limits of detection

Five blank 13-mm diameter, 5-µm pore size polyvinylchloride filters, (SKC Ltd., UK), commonly used for workplace aerosol sampling, were ashed at 600 °C in a furnace, ultrasonicated with isopropanol and filtered onto a 5-mm diameter area on the 0.45-µm pore size silver filters. The measurement strategy was then applied to analyse each of the five silver filters. The total area counts were recorded from any identifiable peaks found in the spectra that matched the quartz or cristobalite wavenumbers. The standard deviation was calculated from the accumulated counts from each of the five filters (Table 2).

These LOD values were compared with a procedure proposed in International Organisation for Standardisation 16258 to calculate an LOD^[8] from the variability of the background scatter. The standard deviation of the background scatter from a fitted trend line was calculated from spectra obtained from 11 randomly selected fields of view on two blank filters. The standard deviation was then multiplied by three times the response trend line coefficients for

quartz, or cristobalite. This provides an estimate of the LOD from the scatter of a scan from a single sampling point. Counting statistics will apply to obtain an LOD for the spectra from 50 sampling points, because the detection of a peak in a scan was also dependent on the subjective judgement of the individual analyst. For a Poisson distribution, commonly employed in counting statistics, a count of four is considered above a background level with a 99% level of confidence,^[17] so the estimated LOD for a single scan was also multiplied by four.

Simulated matrix samples

Mixtures of quartz and cristobalite were prepared by pipetting aliquots from a suspension of standard dust onto the same silver filter using the bespoke apparatus in Fig. S1 to test the performance of the measurement in a more complex situation. In addition, mixtures from suspensions of 20% quartz in hematite and 6% quartz in calcite were also studied to assess how Raman spectroscopy would perform as a quantitative tool in these challenging matrices. The hematite and calcite powders were the same as those previously used in a study of X-ray absorption.^[18] The recorded mass was compared with the theoretical mass of quartz deposited on the silver filter determined from the aliquot volume and the concentration of quartz in the suspension. The 95% level of confidence for each mass loading was calculated from the intermediate measurement precision.

Results and discussion

Variation of the Raman signal intensity of the silicon external standard measurement at the same position was <2% when collected sequentially. Repeatability in different positions within a few minutes was approximately 3%. This variability could be due to the sample not being perfectly flat or the presence of non-RCS dust particles. Precision of the measurement between days was approximately 20%. This large between day variation did not change the results for the mass of RCS because the measured value is corrected for the change in intensity, which is relatively consistent during the analysis. XRD analysis identified a pipetting bias between the samples. This was attributed to the use of an air rather than piston displacement pipette for some of the loadings. The

Table 2. Limits of detection for quartz and cristobalite

Analyte	Quartz mass (µg)	Cristobalite (µg)
Limits of detection from filter measurements	0.049	0.066
Limits of detection calculated from variability of the background scatter	0.020	0.032

measured mass value was verified using inductively coupled plasma atomic emission spectroscopy, and based on this, a correction was made to the theoretical loading value for some of the quartz samples. Figure 2 shows that the calibration over a mass range of 0.25–15 μg for quartz, and 1–10 μg for cristobalite was linear over the analytical range of test samples with a calculated coefficient of determination (r^2) of greater than 0.98. The quartz calibration includes 30 samples from two suspensions, and the cristobalite calibration includes 12 samples from two suspensions. Two quartz samples at 20 and 50 μg were also measured but are not included in the chart. The trend line including these two points with the rest of these data had a coefficient of determination of 0.98 indicating that the relationship between mass and response was potentially linear up to 50 μg . The average number of fields with a quantifiable peak measured at the lowest quartz loading of 0.250 μg was seven (14%).

LOD obtained using Raman spectroscopy

The LODs, determined using a blank filter measurement approach, were compared with an LOD calculated from the variability of the background noise (Table 1). The values given in Table 1 indicate a limit for quantification (the standard deviation multiplied by 10) for the measurement of quartz and cristobalite of approximately 0.066–0.161 and 0.106–0.218 μg , respectively. These values are approximately an order of magnitude less than typical LODs for RCS obtained using the XRD and IR analytical techniques (3–10 μg),

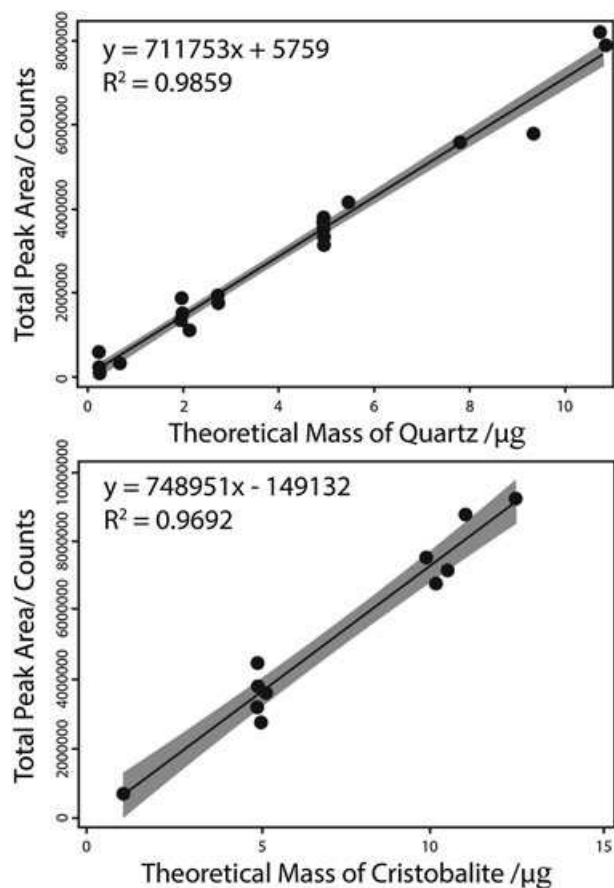


Figure 2. Trend line relationships for Raman response with mass of quartz (NIST 1878) and cristobalite (NIST 1879) loaded in 5-mm diameter area onto silver filters. The shaded area is the 95% confidence interval for each slope coefficient.

which are currently the industry standard for the determination of RCS. Raman microscopy also has the potential to reduce the LODs further by analysing a greater proportion of the sample area, i.e. scans from more sampling points and longer collection times. A calibration in terms of counts/sampling point permits the analyst some flexibility in their measurement approach when analysing samples from challenging low dust concentration environments because they would be able to collect more scans from sampling points to improve the LOD without having to recalibrate for the increase in measured area.

Precision of measurements on test filters

Intermediate precision for the analysis of quartz using Raman microscopy on replicate samples is shown in Fig. 3. The values in Fig. 3, which decrease from approximately 25% to 10% over the mass range of 0.25–10 μg , include a contribution due to pipetting precision and different analysts. An analytical precision of approximately 10% in the range of 2–10 μg is satisfactory for routine work and could be improved by collecting spectra from more fields of view, as some error will be due to the inhomogeneity of the deposit. Figure 3 also demonstrates the benefit of correcting for the laser intensity using the Si external standard. Some additional variability might be due to slight differences in the way the external standard measurement was collected by different researchers, as the intensity of the Si signal using Raman microscopy is dependent upon the sample orientation.

Effect of aerodynamic particle size on measurement response

The differences in measured response between three respirable quartz dust standards (NIST 1878a, A9950 and Quin 1 B) used for calibrations are shown in Fig. 4. The median number aerodynamic particle size values of the NIST 1878a and A9950 reference materials are very similar (1.4–1.5 μm), although A9950 contains a larger proportion of larger diameters by mass (Table S1), and they have different crystallinities (93.7% and 89.3%). Quin 1 B is a powder where its particle size distribution has both larger number and mass median particle sizes (3.2 and 7.1 μm , respectively) when compared with NIST 1878a and A9950 so would be most affected by any changes in Raman response due to particle size differences. The probability (p) that the standards with the largest differences in median aerodynamic diameter (NIST1878a and Quin B) were different was not significant ($p = 0.22$) when trend lines with an intercept were evaluated over the analysis range shown. The

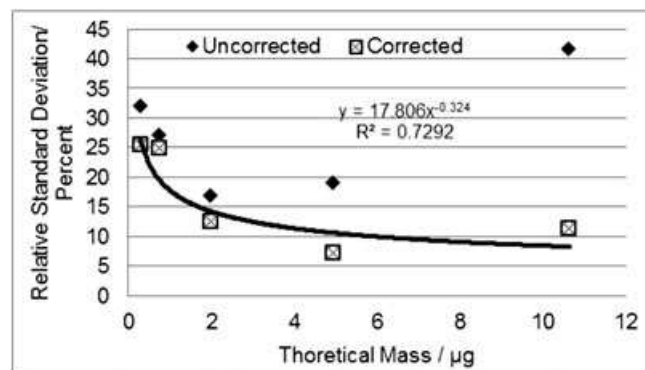


Figure 3. Intermediate measurement precision for Raman measurement of quartz (NIST SRM 1878) deposited into a 5-mm diameter area on silver filters.

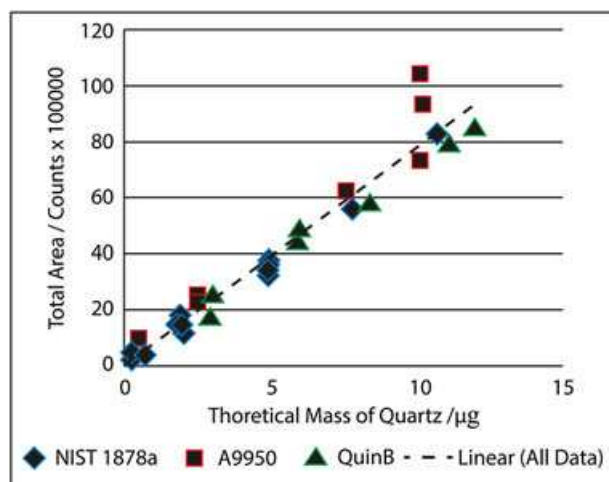


Figure 4. Comparison of the Raman response with mass when measuring respirable quartz calibration dusts NIST 1878a, A9950 and Quin 1B with different median number and mass aerodynamic particle sizes. [Colour figure can be viewed at wileyonlinelibrary.com]

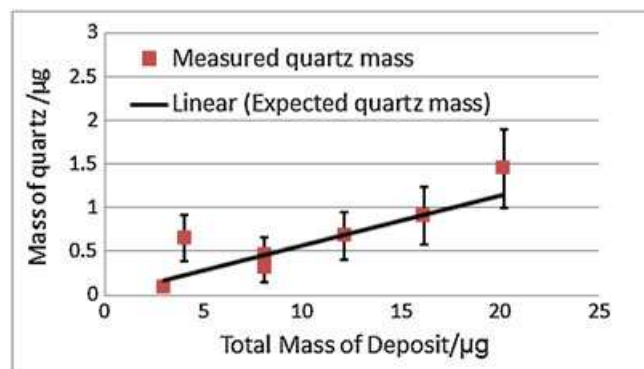
comparison between A9950 and NIST 1878a was borderline significantly different ($p = 0.04$); however, most values were close to the NIST 1878a trend line relationship below $10 \mu\text{g}$ and if a single value at the highest loading is removed the response relationship with mass loading from the two materials is not significantly different ($p = 0.08$). These results demonstrate that the difference in response due to aerodynamic particle size within the respirable size range will not significantly affect the reported result for most samples within the mass range $0.25\text{--}10 \mu\text{g}$. Conversely, XRD and IR measurements are affected by differences in median aerodynamic particle size of the powder within the limited respirable range.^[16] We reason that, when using a quantitative method based on the accumulated Raman spectra from random selection of a number of sampling points, the number distribution of particles is more critical than their mass distribution. In addition, because the test samples are prepared in terms of mass per unit volume, the number of particles per unit mass loaded on these filters is reduced when respirable quartz calibration dusts with larger particles are prepared. This potentially compensates for any change in Raman response because of the larger aerodynamic particle size. It should be noted that 'Quin 1B' is not intended for the preparation of calibration standards prepared from a suspension and represents a larger aerodynamic particle size distribution that would not routinely be expected on a sample filter collected using a respirable size selective aerosol sampler for occupational hygiene sampling.

Results from simulated mixtures

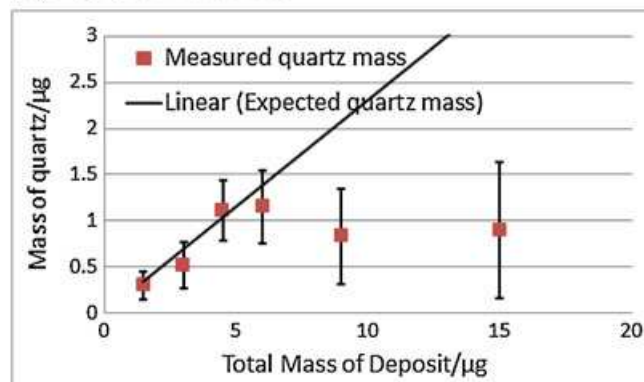
Four mixtures of pure cristobalite and quartz were measured (Table S2). Ratios of measured mass with the theoretical mass for three of the four samples were within 5% for both quartz and cristobalite. The fourth sample, with the highest loading, was slightly high approximately 20%. Measurement of mixtures of quartz and cristobalite were challenging because of the convolution of overlapping peaks within the spectrum (Fig. 1). There were some individual analyte differences where the use of peak fitting and Fourier self-deconvolution approaches may have improved the area measurement but were not used for these experiments.

Results from samples simulating more realistic sample mixtures of 6% quartz in calcite and 20% quartz in hematite are shown in

Fig. 5. The bar with each measurement represents the 95% level of confidence calculated from the intermediate precision. Whereas the calculated mass of quartz in calcite follows the line of expected mass, indicating that Raman would be able to reasonably measure quartz in matrix samples where calcite is a major component, (e.g. cement dust), the measured values obtained for 20% quartz in hematite tail-off when the total mass of deposit are $>5 \mu\text{g}$. This is because hematite is opaque to visible light, meaning that only signal from the surface of the deposits would be observed. Conversely, calcite is transparent to visible light, meaning the Raman signal comes from a greater depth of the deposited particles. The limit of $5 \mu\text{g}$ for hematite containing samples may therefore be an indicator of a critical mass, below which the particle density of the deposit on the filter is sufficiently dispersed not to affect the Raman signal collected from a sampling point. For this reason, Raman might not be a useful technique for heavily loaded samples from environments with high hematite or iron content, e.g. foundry or coal mine dust. Attenuation of signal from hematite and dark particles is not unexpected and is also an issue with XRD and IR analysis.^[7,8,19] There are several strategies to compensate for this. Firstly, the loadings can be managed by reducing sampling times to ensure the total mass is below the critical level. This requires vigilance on the part of the occupational hygienist taking the sample, who is often not the same person analysing the samples. Alternatively, silver filters are also used in XRD analysis as an internal standard to correct for the absorption. The use of an



(a) 6 % Quartz in calcite



(b) 20 % Quartz in hematite

Figure 5. A comparison of the theoretical with the Raman measured mass of quartz in mixtures of (a) calcite and (b) hematite deposited in a 5-mm diameter area on silver filters. The error bars are the 95% confidence intervals for the Raman measurement. [Colour figure can be viewed at wileyonlinelibrary.com]

internal standard in the Raman measurements was not investigated in this work.

Sample analysis strategy

Sample analysis time is critical to a client in terms of cost and promptness of response. Initially, the Raman analysis was performed manually, and each sample took about 2 h to analyse. However, use of software to automatically locate and analyse a sampling point can count twice as many fields in about half the time. Sample analyses times of greater than ½ h are not uncommon in occupational hygiene air sampling work.

The analytical approach most commonly employed in the Great Britain is a direct on-filter analysis in which the filter on which the sample is collected and analysed directly with no additional sample workup.^[7,8] In other methods, the dust from the air sample filter is recovered and redeposited onto an analysis filter for the instrument.^[19] A direct on-air sample analysis approach is preferable as there is less chance for gross errors because of losses of dust from the recovery process. So long as the mass loading is low (<20 µg) and does not contain signal attenuating components, a direct on-filter Raman technique should be possible. A recovery approach might be needed to remove particles affecting the measurement when loading densities of particles are high. Hematite and iron are soluble in dilute acids, and carbonaceous material can be removed through ashing. Various sample preparation approaches were evaluated to ash a number of surrogate realistic samples of dust on 13-mm diameter filters on polyvinylchloride or mixed cellulose ester filters. The amount of material deposited on a filter is a potentially critical factor for accurate analysis using Raman spectroscopy, so a method that efficiently removes the filter material is essential for an indirect analysis approach with a recovery step in the analytical process. The identification of a method to completely dissolve a filter and unwanted material remains an unresolved issue at this stage. An alternative approach for heavily loaded samplers might be to use an aliquot from a suspension of dust recovered from the air sample filter.

Conclusions

This article has demonstrated the potential advantageous application of Raman spectroscopy for quantification of the mass of quartz and cristobalite with an order of magnitude improvement in the LOD compared with those of current industry standard XRD and IR techniques. The improved sensitivity of the Raman spectroscopy method over traditional measurement approaches may offer an improvement in the capability of occupational hygiene exposure monitoring, enabling the development of new approaches for the measurement of low dust concentration environments and potentially the analysis of samples from miniature samplers at low flow rates. A direct on-air-sample filter approach where the sampled dust collected on the air sample filter without the need to recover it onto a separate analysis filter should be possible, but further work is needed. A limiting factor for Raman microscopy is the presence of light absorbing particles such as hematite. The analysis of quartz was limited to a total deposit mass of <5 µg when measured in a mixture of 80% hematite deposited in 5-mm diameter circle.

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Supporting information

Additional Supporting Information may be found online in the supporting information tab for this article.