Talanta 93 (2012) 392–397

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Determination of quartz in bulk materials from workplace environments using X-ray diffractometry and the absorption diffraction method

James A. Hurst

TestSafe Australia – WorkCover NSW, Chemical Analysis Branch, 5A Pioneer Ave., Thornleigh, NSW 2120, Australia

ARTICLE INFO

Article history:
Received 3 January 2012
Received in revised form 15 February 2012
Accepted 22 February 2012
Available online 1 March 2012

Keywords:
XRD
Quartz
Absorption diffraction

ABSTRACT

A method is described for the determination of crystalline quartz in bulk materials from workplace environments as part of occupational hygiene investigations using X-ray powder diffractometry. The absorption–diffraction model was used for quantification with mass absorption coefficients for samples being experimentally determined using an absorption cell placed in front of the diffracted beam anti-scatter slit. The method was found to be reliable for samples containing from 0.5 to 100 wt.% crystalline quartz, where mass absorption coefficients did not exceed 120 $\text{cm}^2\,\text{g}^{-1}$. Repeatability studies found that mass absorption coefficient determinations and crystalline quartz determinations were both generally within 1–2% relative standard deviation. The method was assessed for accuracy and found to be within 2% absolute when a National Institute of Standards and Technology (NIST) quartz certified reference material (SRM1879a) was analysed. The technique was compared to an internal standard procedure and a paired students *t* test showed that there was no significant statistical difference between the two methods at the 95% confidence level where the *t* value was found to be 0.40 ($p > 0.05 = 0.69$) and the *t* critical value being $t_{\text{crit},0.05,29} = 2.05$. The method was suitable for a variety of matrixes including those containing amorphous material and could be routinely applied to most samples of occupational interest.

1. Introduction

Crystalline quartz is a hazardous substance encountered in workplace situations involving mining, tunnelling, cutting and extraction of many minerals, and various manufacturing processes including ceramic materials and sometimes in foundry operations when used for sand blasting. The main variety encountered is α-quartz also known as low quartz or simply as quartz. When inhaled, the respirable fraction of crystalline quartz may cause a pulmonary fibrosis commonly know as silicosis. Of all the pneumoconioses it is the most severe [1]. Furthermore, respirable quartz is listed as an A2 category or suspected human carcinogen [2]. Materials that contain equal to or greater than 0.1 wt.% crystalline quartz are classified using the R49 risk phrase which states that they may cause cancer by inhalation [3]. This information is necessary when preparing material safety data sheets (MSDS). It is therefore necessary to quantify the content of crystalline quartz in bulk material as part of occupational hygiene investigations. Such bulk samples may be mostly crystalline in nature or contain some amorphous material and come from a variety of sources thereby producing variability in matrixes and interferences.

X-ray powder diffractometry (XRD) offers a means by which the content of crystalline quartz in bulk material can be determined. A number of quantitative analytical approaches are available but can generally be divided into individual reflection methods or whole pattern methods. For individual reflection methods, the approaches include the absorption–diffraction method also known as the external standard method, method of standard additions, internal standard method and reference intensity ratio method (RIR) [4]. For whole pattern methods the Rietveld program is currently one of the main quantification procedures used. With the exception of the absorption–diffraction method all the other techniques require that the sample be mixed with another crystalline phase. This can be either the analyte of interest as for the method of standard additions or an appropriate internal standard such as fluorite, or corundum if the RIR method is used. Even the classical Rietveld approach may require the addition of another crystalline material to correct for amorphous material or when other crystalline phases are present but not in the database. There are however, established methods for quantitative phase analysis when crystal structures are not available [5]. The absorption diffraction method does not require the addition of another crystalline phase for amorphous material correction, or internal standard for absorption correction. There is also no need to know what other crystalline phases are present unless they constitute an overlapping interference. It presents a simple quantitative model as follows [6]:

$$X_s = \frac{I_{(h\,k\,l)\alpha}(\mu/\rho)_s}{I_{0(h\,k\,l)\alpha}(\mu/\rho)_\alpha} \tag{1}$$

E-mail address: james.hurst@workcover.nsw.gov.au

0039-9140/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2012.02.060

where $I_{0(h\,k\,l)\alpha}$ is the intensity of the peak in the pure phase, $I_{(h\,k\,l)\alpha}$ is the intensity of the peak in the phase in the sample, $(\mu/\rho)_\alpha$ is the mass absorption coefficient (MAC) for the pure phase, $(\mu/\rho)_s$ is the MAC of the sample and X_s is the fraction of the phase of interest in the sample. Note that the MAC is independent of the physical state (solid, liquid or gas) of the material for a given wavelength and comprises the linear absorption coefficient μ and the density ρ.

One of the main problems that influences the diffraction line intensity is the different mass absorption characteristics of the sample matrix. The general relationship between the transmitted X-ray intensity and absorbing nature of a sample is given by the following equation (related to the Beer–Lambert law used in UV–vis analysis) [6]:

$$I = I_0 e^{-(\mu/\rho)\rho\chi} \tag{2}$$

where I is the transmitted X-ray intensity (c s^{-1}), I_0 is the beam intensity before entering the absorber (c s^{-1}), (μ/ρ) is the MAC (cm^2 g^{-1}), ρ is the density (g cm^{-3}) and χ is the absorbing layer thickness (cm). Note that the product $\rho\chi$ becomes the mass per area of the absorber (g cm^{-2}). In some cases the MAC for samples and standards are the same. This though, is not generally the case. More commonly the MAC for various samples will be different. Moreover, within standard calibration curves the overall MAC for each standard will be different and the resulting calibration line will deviate from linearity. Therefore, the MAC needs to known. It can be calculated using published MAC values and known sample chemistry. This can be done by using the known MAC values for the components and simply adding up the fractions of each. The general formula for calculating MAC is given by the following equation [7]:

$$\left(\frac{\mu}{\rho}\right)_t = w_1\left(\frac{\mu}{\rho}\right)_1 + w_2\left(\frac{\mu}{\rho}\right)_2 + \ldots + w_n\left(\frac{\mu}{\rho}\right)_n \tag{3}$$

where $(\mu/\rho)_t$ is the total MAC for the sample mixture, w_1 is the weight fraction of component 1, $(\mu/\rho)_1$ is the MAC for component 1, w_n is the weight fraction of the nth component and $(\mu/\rho)_n$ is the MAC of the nth component. If the sample chemistry is not known then the MAC needs to be experimentally determined. It can be determined by using indirect XRF techniques and methods based on the inverse relationship between MAC and X-ray tube Compton scatter intensity [8]. Other methods have used direct absorption measurements using an X-ray spectrometer that had provision for an absorption cell in front of the scintillation detector collimator via a small opening in the X-ray spectrometer cabinet [9,10]. Such measurements were carried out using pressed boric acid discs with and without sample that were placed in an absorption cell to measure the fluorescent radiation from a target disc with the goniometer set at the appropriate wavelength.

By rearranging Eq. (2) the MAC for the sample could be calculated using the following equation:

$$\left(\frac{\mu}{\rho}\right) = \frac{\ln(I_0/I)}{\rho\chi} \tag{4}$$

Having determined a value for the MAC (μ/ρ) this value was used in the absorption diffraction method equation (1) for determining the fraction of a phase in a bulk sample. Due to safety concerns with regard to exposure to X-ray radiation modern X-ray spectrometers no longer have the capability to place as sample in an absorption cell in front of the scintillation detector.

Another approach is to use an XRD instead of an XRF for making MAC measurements using either substrate diffraction techniques [11] or direct measurements on pressed powders [4]. In early work, direct MAC determinations were made but the radiation was not altogether monochromatic [12]. Carrying on from this, monochromatic radiation was used to measure MAC by mounting a thin specimen in front of the diffracted beam receiving slit (DBRS) and measuring the attenuation of the beam from a single-crystal quartz slab in the sample position. Copper radiation was used for most samples and cobalt used when samples contained large amounts of iron. This method was applied to clay minerals where the authors claim a general reproducibility of about 1% [13]. Other workers also applied this type of method to the composition of shales and attained accuracies for phase quantification of ±10% [14]. Whilst the authors of this early work state that these methods are satisfactory, the absorption diffraction method seems to have fallen out of favour and few if any current applications use it. This may be because errors of direct measurement in MAC using conventional powder diffractometers are too large for the technique to be useful on certain types of sample [6,15] and as stated earlier the Rietveld approach seems to be the dominant technique used for multiphase quantification whereas for single phase quantification the internal standard method is commonly used.

The main aim of this article is to demonstrate that a simple modification of an existing XRD Bragg–Brentano θ:θ goniometer can be used to determine sample MAC directly that are both accurate and reproducible and when using the absorption diffraction method a viable and comparable alternative to other quantification models is possible. When only one phase is of interest and samples are of a relatively low absorbing nature or contain a significant amount of amorphous material the method is satisfactory. The approach is that an incident beam of CuKα radiation would strike a sample of pure α-quartz with the resulting diffracted beam converging on an absorption cell mounted in front of the diffracted beam programmable anti-scatter slit (PASS). The X-rays after travelling through this absorption cell would enter a Soller slit prior to reaching the detector. The diffracted X-rays would be produced from the pure quartz sample and a stationary measurement used to collect counts from the main Q101 line. The intensity for this peak would be recorded for blank and samples loaded into the absorption cell. The MAC values would be determined for various samples from workplace situations and these MAC values applied using the absorption diffraction calibration model.

2. Experimental

2.1. Reagents and materials

The reagents used were Analytical Reagent grade α-quartz (Merck) washed and calcined, Cellulose Ashless Powder CL-170 (Choice Analytical), boric acid (APS Finechem) 99.5% minimum and calcium fluoride as fluorite (APS Finechem) 96% minimum. A Fritsch Pulverisette 6 ball mill was used to grind and mix samples. A Sartorius model 160D analytical balance was used with a resolution of ±0.00001 g. Ground specimens were pressed using a Specac manual press. A special die set (Philips PW1416/20) was used which consisted of piston, sleeve, base plate ring and base plate. See Fig. 1. Perspex sample holders consisted of a 3 mm thick rectangular piece of the plastic approximately 30 mm × 75 mm in size. A hole was cut down one end where the pressed sample would be loaded. The base plate ring of the die set had a slot to insert the Perspex sample holders. The cross sectional area of the hole cut in the Perspex was 3.6 cm^2. PANalytical PW1811/27 powder sample holders were used and loaded using a PW1770/10 sample preparation kit.

2.2. Instrumentation

A PANalytical X'Pert Pro system was used. The instrumental conditions are shown in Table 1. In front of the PASS was a bracket for holding Perspex sample holders for mounting samples for MAC determinations. This absorption cell was made from polycarbonate plastic and consisted of two 50 mm diameter discs with a 30 mm

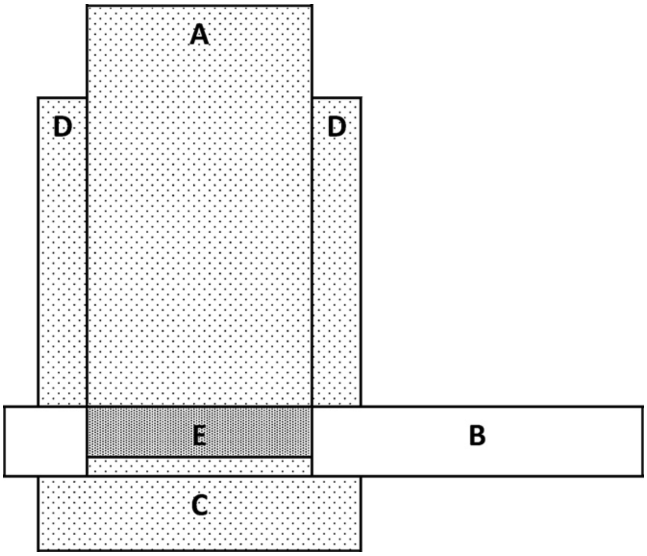

Fig. 1. Schematic of die assembly used to press specimens for MAC determination. (A) Piston, (B) perspex sample holder in base plate ring, (C) base plate, (D) sleeve and (E) sample.

diameter hole cut out from the centre of both discs. The discs were 5 mm thick and mounted together in line with a 3.5 mm space between them. This arrangement was positioned in front of the PASS using four small screws that could be fitted into the existing threaded holes in the front of the PASS. The Perspex sample holder was placed between these discs and in line with the diffracted X-ray beam. See Fig. 2. All measurements were collected using X'Pert Data Collector for the MAC determination and X'Pert Quantify for the quartz determination. Qualitative search match routines were carried out using X'Pert Highscore and the International Centre for Diffraction Data (ICDD) PDF4+ database.

2.3. Mass absorption coefficient (MAC) determination

The empty perspex sample holder was taken and accurately weighed to 4 decimal places using a Sartorius analytical balance. It was then mounted in the absorption cell in front of the XRD detector. A stationary measurement was made on a sample of α-quartz at the Q101 peak angle for 100 s. The gross counts for the peak were recorded as I_0. The holder was removed and mounted in the die. To the die was added approximately 0.3 g of sample that had been previously diluted and mixed with cellulose at a ratio of 0.1–1.0 g of sample to 4 g of cellulose in a Fritsch P6 mill at 300 rpm for 15 min. The ground sample was evenly distributed across the bottom of the die. The piston was inserted and rotated gently to even out the sample distribution. The Perspex holder containing diluted sample was mounted in the Specac press and a load of 2 tonnes applied for 10 s. The Perspex sample holder was removed and accurately weighed to 4 decimal places using a Sartorius analytical balance. The Perspex sample holder was then taken and mounted in the absorption cell in front of the XRD detector. A stationary measurement was made on a sample of α-quartz at the Q101 angle for 100 s. The gross counts for the peak were recorded as I. The MAC was calculated using Eq. (4). For the particular Perspex sample holder used the mass of the

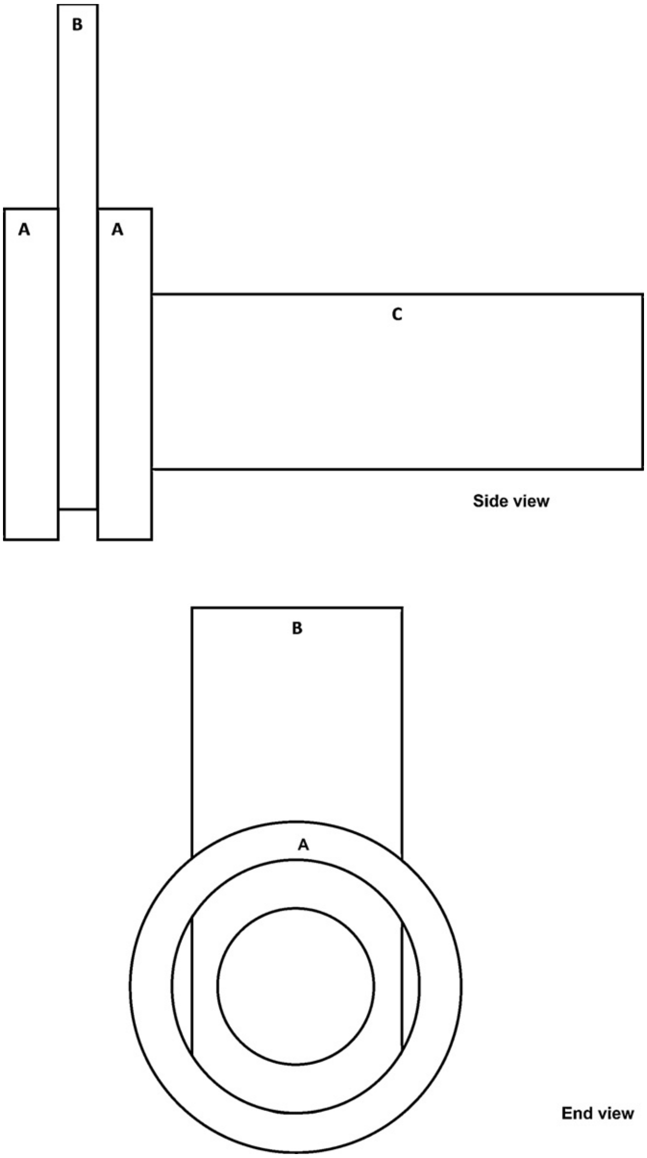

Fig. 2. Schematic of absorption cell used to measure MAC. (A) Mounting ring, (B) perspex sample holder containing sample and (C) programmable anti-scatter slit (PASS).

Table 1
X'Pert PRO XRD system instrumental settings.

Incident beam optics	Sample platform	Diffracted beam optics
CuLFF Tube 45 kV 40 mA (0.154 nm) Radius 240 mm Soller slit 0.04 rad Programmable divergence slit (20 mm irradiated length) Mask 15 mm (17 mm constant beam width)	Sample spinner (2 s/revolution) Sample changer	Radius 240 mm Programmable anti-scatter slit (20 mm irradiated length) Anti-scatter shield Soller slit 0.04 rad Nickel filter X'Celerator detector 2.17 mm active length Receiving slit mode (MAC determination) 2.122° active length Scanning mode (quartz determination)

pellet i.e. $\rho\chi$ was calculated by subtracting the blank Perspex holder weight from the same Perspex holder weight containing the sample. This gave the weight of sample in grams. This value was divided by 3.6 (this was the area of the pellet produced in cm^2) to give the mass per area of the pellet in g cm^{-2}. A correction factor was then required to account for the original sample dilution with cellulose.

This was calculated using the following equation [16]:

$$\left(\frac{\mu}{\rho}\right)_s = \frac{(\mu/\rho)_f - (1-P)(\mu/\rho)_d}{P} \quad (5)$$

where $(\mu/\rho)_s$ is the corrected MAC for the sample, $(\mu/\rho)_f$ is the uncorrected or found MAC, P is the fraction of sample in the mixture and $(\mu/\rho)_d$ is the experimentally determined MAC of the diluent.

2.4. α-Quartz determination

A series of standards were prepared by mixing known amount of quartz with fluorite. These standards were 0, 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 wt.% added α-quartz in fluorite. They were ground and mixed in a P6 mill at 300 rpm for 15 min to minimise particle size effects and backfilled into PANalytical PW1811/27 powder sample holders using a PW1770/10 sample preparation kit. The samples were lightly pressed by hand. The calculated MAC for the standards is found in Table 2. The values for each standard were entered and data collection was performed by measuring a scan from 10° to 60°2Θ. The peak areas collected for the quartz standards were (1 0 0) (20.9°2Θ), (1 0 1) (26.7°2Θ), (1 1 2) (50.2°2Θ) and (2 1 1) (60.1°2Θ). They were then isolated from the scan using the X'Pert Quantify software data acquisition program. After all the standards were run calibration lines for each of the four quartz peaks were constructed and the calibration constants were determined based on the following equation known as the general model in the X'Pert Quantify software with MAC values for standards calculated according to Eq. (3).

$$C_i = I_i B_i \left(\frac{\mu}{\rho}\right)_s \quad (6)$$

where C_i is the concentration of α-quartz in the sample in (wt.%), I_i is the peak area intensity in (c s^{-1}) and B_i the calibration constant (slope^{-1}) in (wt.% s c^{-1} g cm^{-2}). An aluminium monitor specimen was also run and used to correct for instrumental drift by making slope corrections to the calibration lines. Unknown samples were firstly ground in a P6 mill at 300 rpm for 15 min. They were then prepared in a similar fashion to the standards in that they were back filled using the PW1770/10 sample preparation apparatus. This back filling was done to help minimise orientation effects. Having experimentally determined the MAC for the unknowns these results were entered into the appropriate software field and the unknowns run from 10° to 60°2Θ and a quantitative result generated. This scan was also used to identify any interfering crystalline phases present by using a search match routine and the ICDD PDF4+ database.

Table 2
Calculated MAC for standards.

α-Quartz (g)	Fluorite (g)	MAC (cm^2 g^{-1})
0	10.0067	91.95
0.1049	9.9065	91.35
0.5105	9.4561	89.02
1.0006	9.0021	86.24
2.0053	8.0075	80.51
3.0021	7.0073	74.82
4.0002	6.0029	69.11
5.0140	5.0037	63.37
6.0026	4.0013	57.68
7.0050	3.0054	51.99
8.0275	2.0080	46.27
9.0374	1.0034	40.55
10.0223	0.0000	34.84

3. Results and discussion

3.1. Mass absorption coefficient (MAC) determination

Three types of approach were investigated when determining the sample MAC. The first involved pressing the sample directly with no binder, diluent or backing. This approach was found to be satisfactory for low absorbing organic materials where the MAC was generally less than about 20 cm g^{-1} only. For intermediate absorbing materials of a silicate nature a boric acid backing was required. This was required because it was difficult to prepare a stable and yet thin enough specimen for measurement. This approach was found to be satisfactory for MAC up to around 70 cm g^{-1}. For highly absorbing materials a dilution with a low absorbing material was required. This was finally chosen as the preferred method and samples were mixed with cellulose at dilutions of 1 in 5. This was found to be suitable for MAC up to 120 cm g^{-1}. For more absorbing samples larger dilutions would be required. A number of measurements were carried out to investigate if the experimentally determined MAC were in agreement with reference values. The reference values were based on those from the international tables for X-ray crystallography [17]. Compounds were chosen such that the MAC values ranged from 4 to 260 cm g^{-1}. The results are presented in Table 3. From the results obtained it can be seen that there is general agreement between the reference value and the experimentally determined value. The lower MAC compounds tend to give better results and most are around within 2–4% of the reference value. For MAC values greater than 120 cm g^{-1} the experimental value is less than the reference value. This may be the result of difficulty in preparing highly absorbing specimens in a thin enough form and further dilution would be required.

3.2. α-Quartz determination

Having calculated the MAC values they were then used in the α-quartz determination using Eq. (6). The calibration curve constructed using the mixed standards of α-quartz and fluorite produced a straight line with a coefficient of determination of $r^2 = 0.999$. Plots of the residuals of the calibration indicated that the graph was linear and the variance of data was independent of the concentration and therefore homoscedastic i.e. constant standard deviation. Additionally, none of the residuals exceeded 3 times the standard error of the calibration indicating that outliers were not present The most intense diffraction line was used

Table 3
Measured MAC compared with reference (calculated) MAC.

	Measured MAC (cm^2 g^{-1})	Reference MAC (cm^2 g^{-1})	Dilution factor
Tetradecanol	4.24	4.24	1
Hexamine	5.26	5.08	1
Phthalic acid	6.91	6.71	1
Starch	7.60	7.33	1
Boric acid	8.95	8.92	1
Sodium carbonate	14.8	14.8	1
Sodium oxalate	15.5	15.9	1
Zinc acetate	22.9	23.6	1
Quartz	34.8	34.8	1
Calcium carbonate	69.2	71.5	1
Sulfur	90.1	89.7	5
Potassium bromide	105.0	106.4	5
Potassium chloride	118.4	121.5	5
Barium carbonate	237.0	244.2	50
Potassium iodide	239.0	263.9	50

for quantification. This being the Q101 α-quartz line unless interferences were suspected in which case a less intense line was used.

Based on the results of the calibration model as used in Eq. (6) the slope was found to be 1052.4 c s^{-1} cm^2 g^{-1} wt.%$^{-1}$ with the calibration line forced through zero. In addition, the root mean square or average deviation is given to describe the quality of the calibration or goodness of fit [18]. The equation being:

$$\mathrm{RMS} = \sqrt{\frac{1}{n-k}\sum (C_{chem} - C_{calc})^2} \tag{7}$$

where RMS is the root mean square deviation in wt.%, C_{chem} is the known amount of α-quartz in the standard in wt.%, C_{calc} is the amount of α-quartz calculated from the regression line in wt.%, n is the number of standards used in the calculation (in this case $n = 11$) and k is the number of calculated constants i.e. slope and y intercept. Although, in the calibration used the line was forced through zero hence k will be 1. The RMS value was calculated to be 1.3 wt.% across the calibration range.

The statistical limit of detection (LOD) was calculated by making measurements on a standard of 0 wt.% α-quartz in Fluorite using the Q101 peak and using the following formula:

$$\mathrm{LOD} = \frac{3.3s}{m} \tag{8}$$

where LOD is the statistical detection limit in wt.%, s is the standard deviation of the response of 10 measurements of a α-quartz free fluorite sample in c s^{-1} (0.57 c s^{-1}) and m is the slope in c s^{-1} wt.%$^{-1}$ corrected for the MAC and obtained from the calibration line (30.2 c s^{-1} wt.%$^{-1}$). The LOD was found to be 0.1 wt.%. A reasonable limit of quantification would be expected to be around 0.5 wt.% for the most intense Q101 α-quartz line in an interference free matrix and where the MAC is not greater than 120 cm g^{-1}.

3.3. Repeatability

The method was assessed for repeatability. The two aspects investigated were MAC determination and quartz determination. For the MAC determination three compounds were chosen, α-quartz ($\mu/\rho = 34.84$ cm g^{-1}), calcite ($\mu/\rho = 71.5$ cm g^{-1}) and potassium chloride ($\mu/\rho = 121.5$ cm g^{-1}). Mixtures of these compounds were taken, pressed, loaded and measured in the absorption cell. This process was repeated 10 times for each compound. For α-quartz the mean MAC was found to be 34.8 cm g^{-1}, with a standard deviation (s) of 0.4 cm g^{-1} and relative standard deviation (RSD) of 1.2%. For calcite the mean MAC was found to be 69.2 cm g^{-1}, with a s of 0.8 cm g^{-1} and RSD of 1.1%. For potassium chloride the mean MAC was found to be 118.4 cm g^{-1}, with a s of 2.0 cm g^{-1} and RSD of 1.7%.

The next aspect of repeatability was the quantification of α-quartz using the Q101 line. This was determined at the 1, 50 and 100 wt.% quartz in fluorite levels. The RSD were found to be 4.9%, 0.2% and 0.1%, respectively. The absolute standard deviations were found to be 0.05%, 0.1% and 0.1%, respectively at the three levels indicating that the variance of data was independent of the concentration and therefore homoscedastic i.e. constant standard deviation.

3.4. Method performance

The method is suitable for materials where the MAC of the sample contains low amounts of iron and is less than 120 cm g^{-1}. For samples containing large amounts of iron a diffracted beam monochromator would be needed or Cobalt tube used. The method was generally found to be within 2–4% relative when determining the MAC.

For synthetic mixtures of α-quartz in fluorite the accuracy of the quantification procedure using the absorption diffraction method as determined by absolute differences ranged from 0.3% at the 1 wt.% quartz level to 2% at the 90 wt.% quartz level. Relative differences ranged from 26% at the 1 wt.% α-quartz level to 2% at the 90 wt.% quartz level. An AR Fluka α-quartz powder sample was also analysed. The α-quartz result obtained was found to be 96 wt.% whereas the result for a Merck α-quartz standard when run as unknown was found to be 98 wt.%. Hence the two α-quartz materials from different suppliers gave similar results. Certified reference materials (CRMs) containing assayed levels of α-quartz in a variety of matrixes are not generally available. However, a CRM for the determination of respirable α-quartz is available from the National Institute of Standards & Technology (NIST) and designated SRM1878a with a certified reference value of 93.7 ± 0.21 wt.% crystalline α-quartz. This was analysed and found to contain 92.5 wt.% α-quartz. All these values are consistent with reasonable expectations whereby absolute accuracy levels of around 2 wt.% can be achieved under ideal XRD conditions [19]. In addition, a study using an internal standard technique found average quartz values of less than 1% deviation from actual values when artificial shales were analysed in the 3–35 wt.% α-quartz range [20]. These results are also similar to a study of clay minerals in sandstone that compared Rietveld to the RIR method and found results accurate to ±3 wt.% absolute (including α-quartz) for both techniques [21]. Note that in the Rietveld method if amorphous material is present and a correction is not undertaken for this then results will be normalised to 100 wt.% and an overestimation of quartz made.

Another limitation of XRD methods is that interfering phases can produce line overlaps. Fortunately, there are four main α-quartz lines (1 0 0), (1 0 1), (1 1 2) and (2 1 1) that can be used for quantification. If an overlap is suspected one of the interference free lines can be used with however, a reduced limit of detection. Common interferences are presented in Table 4 [22]. If on the rare occasion all 4 quartz lines are subject to interference and the interference can be identified it may be possible to make a correction based on the relative intensity relationship between another of the interference lines and the interfering line on the quartz peak. There is also the possibility to take the average quantification values of the four quartz peaks when interferences are not present thereby improving the result if orientation effects are suspected. In addition, because the absorption diffraction method does not require the addition of another crystalline phase as in the case of the internal standard method the problem of unknown matrixes and any overlaps on the internal standard peak are not encountered. Another advantage of the absorption diffraction method is that the analytical sample

Table 4
Commonly encountered line overlaps associated with quartz.

	(1 0 0)	(1 0 1)	(1 1 2)	(2 1 1)
Albite	–	O	O	O
Anorthite	O	O	–	–
Aragonite	O	O	O	O
Biotite	–	O	–	O
Graphite	–	O	–	O
Gypsum	O	–	O	–
Kaolinite	O	O	O	O
Maghemite	O	O	O	–
Nucricline	O	O	–	–
Mullite	–	O	–	O
Muscovite	–	O	–	–
Sillimanite	–	O	O	O
Vaterite	O	O	O	O
Wollastonite	–	O	O	O
Wustite	–	–	–	O
Zircon	–	O	–	O

Where: O: potential overlap, –: no overlap.

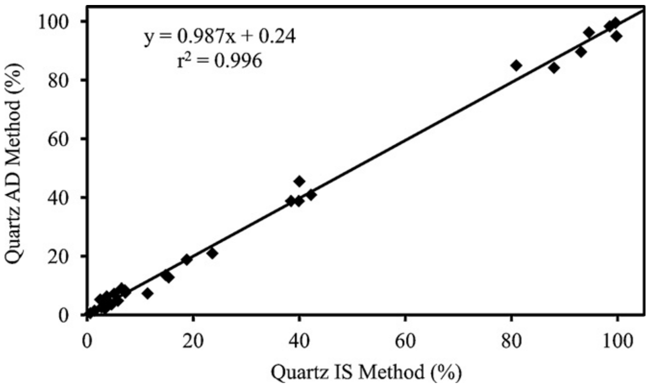

Fig. 3. Results for quartz using absorption–diffraction method (AD) compared with internal standard method (IS).

used for quantification is not mixed with another phases that will contaminate it if it needs to be further analysed by another technique. A small amount of the sample is however, used for the MAC determination when mixed with cellulose.

3.5. Application and evaluation

The method was applied to a number of samples ($n = 30$) submitted to this laboratory from workplace environments. The types of material analysed included clay minerals and other materials with major matrix phases such as talc, calcite, dolomite, kaolinite, quartz and coal type matrixes. These materials were analysed using the proposed method and compared with a standard calibration based on the internal standard technique using fluorite as the internal standard in a variable concentration model. The standards used to prepare the calibration for the internal standard method were the same as used to calibrate the XRD for the absorption diffraction method. This was done to minimise the standards as a source of systematic error in the comparison. Samples were mixed with fluorite by accurately weighing 8 g sample and 2 g fluorite. A correction factor of 1.25 was applied to the results to allow for the dilution. A plot of the results for the absorption diffraction method versus the internal standard method is given in Fig. 3. The internal standard method was considered the reference method in the comparison. The coefficient of determination was calculated and found to be $r^2 = 0.996$. Note that r^2 values only give information about relationship strength and do not show that methods are the same nor indicate linearity. From this plot information about proportional error (slope), constant error (intercept) and random error in y direction (standard error) were also determined. The slope was found to be 0.987, the intercept 0.24 wt.% and the standard error 2.39 wt.%. In order to determine if a linear relationship model was appropriate for this comparison a plot of the residuals versus concentration was made. The resulting plot showed that the points were randomly distributed about the x-axis indicating that a linear model was appropriate. The next step involved calculating the s for the slope and intercept [23]. The s for the slope was calculated to be 0.012 and the s for the intercept was found to be 0.58 wt.%. Hence, the slope could be expressed as 0.987 ± 0.025 and the intercept 0.24 ± 1.19 wt.% at the 95% confidence limits where $t_{0.05,28} = 2.05$ (n-2 degrees of freedom) was the value used. In addition, because the calculated confidence limits for the intercept include 0, and the slope includes unity this indicates that there is no systematic bias between the two methods.

Furthermore, it can be seen from Fig. 3 that if the two methods were identical then the slope should be unity and the intercept 0. However, the slope was found to be less than unity and the intercept greater than 0. This therefore required the calculation of t values for slope and intercept and comparing them to the t critical value to assess if these systematic differences were statistically significant. The t values for slope and intercept were calculated to be 1.07 ($p = 0.29$) and 0.41 ($p = 0.69$) respectively. When compared to the two tail t critical value of $t_{\text{crit},0.05,28} = 2.05$ (n-2 degrees of freedom) it was concluded that the slope was not significantly different from unity and the intercept not significantly different from 0. Hence, the methods were not dissimilar.

A paired students t-test was also undertaken of the results. There was found to be no significant statistical difference between the absorption diffraction method and the internal standard method at the 95% confidence limits where the t value was found to be 0.40 ($p > 0.05 = 0.69$) and the t critical value being $t_{\text{crit},0.05,29} = 2.05$ (n-1 degrees of freedom).

4. Conclusions

From the proposed method it was observed that whilst the absorption diffraction procedure may have some limitations when highly absorbing compound are present it is still useful for measuring α-quartz in bulk samples from a variety of workplace situations. It was found to be suitable for both crystalline and amorphous samples with results comparable to existing methods such as the internal standard procedure.

Acknowledgements

The author would like to thank Dr. Greg O'Donnell (Laboratory Manager) and John Volpato (Analytical Chemist) for their advice in the preparation of this paper.

References

[1] L. Parmeggiani (Ed.), Encyclopaedia of Occupational Health and Safety, International Labour Organisation, Geneva, 1983, pp. 2036–2041.
[2] American Conference on Governmental Industrial Hygienists (ACGIH), 2010 TLVs and BEIs, ACGIH, Cincinnati, 2010.
[3] Approval Criteria for Classifying Hazardous Substances [NOHSC: 1008], Canberra, Aust Govt Publishing Service, Canberra, 1994.
[4] R. Jenkins, R.L. Snyder, Introduction to X-Ray Powder Diffractometry, John Wiley & Sons, New York, 1996.
[5] N.V.Y. Scarlett, I.C. Madsen, Powder Diffr. 21 (2006) 278–284.
[6] H.P. Klug, L.E. Alexander, X-Ray Diffraction Procedures for Polycrystalline and Amorphous Materials, John Wiley & Sons, New York, 1974.
[7] B.D. Cullity, Elements of X-Ray Diffraction, Addison-Wesley, Reading, MA, 1978.
[8] R.C. Reynolds, Am. Mineral. 46 (1963) 1133–1143.
[9] K.L. Williams, An Introduction to X-Ray Spectrometry: X-Ray Fluorescence and Electron Microprobe Analysis, Allen & Unwin, London, 1987.
[10] Philips Corporation, Manual Vacuum X-Ray Spectrometer and Accessories PW1410/00, Philips Gloeilampenfabrieken, Eindhoven, 1970.
[11] B.L. Davis, L.R. Johnson, Adv. X-Ray Anal. 333 (1986) 333–342.
[12] J. Leroux, D.H. Lennox, K. Kay, Anal. Chem. 25 (1953) 740–743.
[13] K. Norrish, R.M. Taylor, Clay Min. Bull. 5 (1962) 98–109.
[14] D.B. Shaw, C.B. Weaver, J. Sediment. Petrol. 35 (1965) 213–222.
[15] M. Kahle, M. Kleber, R. Jahn, Geoderma 109 (2002) 191–205.
[16] A.C. Moore, Am. Mineral. 54 (1969) 1180–1189.
[17] International Tables for X-Ray Crystallography, vol. C, Mathematical, Physical and Chemical Tables, Kluwer, London, 1995.
[18] Philips Corporation, X44 Software for XRF Operation Manual, Philips, Eindhoven, 1990.
[19] D.K. Smith, International Symposium Issues and Controversy: The Measurement of Crystalline Silica. Evaluation of the Detectability and Quantification of Respirable Crystalline Silica by X-Ray Powder Diffraction, The Pennsylvania State University, Pennsylvania, 1992, pp. 39–40.
[20] J. Srodon, V.A. Drits, D.K. McCarty, J.C.C. Hsieh, D.D. Eberl, Clays Clay Miner. 49 (2001) 514–528.
[21] S. Hillier, Clay Miner. 35 (2000) 291–302.
[22] Health and Safety Executive (HSE), Methods for the Determination of Hazardous Substances: MDHS 101: Crystalline Silica in Respirable Airborne Dusts, HSE Books, Sudbury, 2005.
[23] D.B. Hibbert, J.J. Gooding, Data Analysis for Chemistry, Oxford, New York, 2006.