The Effect of Size-selective Samplers (Cyclones) on XRD Response

C.J. PRETORIUS
Council for Scientific and Industrial Research, South Africa

ABSTRACT: The study evaluated five size-selective samplers used in the South African mining industry to determine how their performance affects the X-ray powder diffraction (XRD) response when respirable dust samples are analysed for quartz using direct-on-filter XRD. The samplers' performance was analysed with three test dusts in an aerosol dust chamber as described in MDHS 101. The performance of size-selective samplers was found to affect the XRD response during quartz analysis and the quartz concentration measured. The performance of each sampler also changed when a different type of dust was used. Factors contributing to the XRD response were the distribution of dust on the filter, the particle size distribution of the dust sampled and the performance of the sampler. Recommendations are that a national sampler be used during the sampling of airborne dust at mines and at laboratories and that a national quality assurance protocol be developed to evaluate the sampler.

1 INTRODUCTION

Among the hazards mine workers are exposed to in airborne dust, crystalline silica (alpha-quartz) is particularly hazardous as it causes silicosis, a debilitating lung disease. So that measures can be taken to prevent worker exposure to this hazard it is necessary for the South African mining industry to obtain accurate measures of the amount of crystalline silica in the airborne dust in mines. The conventional method used in the South African mining industry to determine the concentration of respirable silica-containing dust is through the use of a sampling pump with a size-selective sampler and filter media. The fraction of airborne dust that is sampled is the respirable fraction where the dust particles are smaller than ten micron.

The filter medium onto which the respirable dust is collected is sent to a laboratory for analysis, where the techniques most commonly used for measuring the concentration of silica in the dust are X-ray powder diffraction (XRD) and Fourier-Transform Infrared (FTIR). Both techniques are susceptible to factors which have an effect on the accuracy of the silica result, particularly, in the case of the XRD result, the manner in which the size-selective sampler gathers dust and deposits the dust onto the filter medium.

The requirements for samplers used to sample respirable dust are that they should comply with the specifications set out by the American Conference of Governmental Industrial Hygienists (ACGIH), International Organization for Standardization (ISO), and European Standard Committee (CEN), which state that such a sampler should have a dust-collection efficiency curve where the 50% cut-point is 4 μm.

A recent study to determine the particle-capturing performance of two locally manufactured size-selective samplers (Pretorius 2010) found that the samplers (i.e. cyclones) remove not only the respirable fraction of the dust from the airborne dust but also particles of much larger than ten micron. The implication is that when the respirable dust sample is analysed using XRD the silica concentration is overestimated.

The 2010 study was the departure point for the current study, which was undertaken to evaluate all the samplers available to the South African mining industry and make recommendations to industry about a national sampler and a possible test protocol, which South Africa lacks at present.

2 OBJECTIVES

The aim of this study was to evaluate five size-selective samplers available to the South African mining industry and to determine how their performance affects the XRD response when respirable dust samples are analysed for quartz using direct-on-filter XRD. The intention of the study was to look at the resulting respirable dust sample, how the dust was distributed on the filter, what the particle size distribution (PSD) of the dust was and how this affected the analysis of quartz using XRD.

3 METHODOLOGY

3.1 Samplers Used

A questionnaire was sent out to over 30 mines to determine which size-selective samplers are most commonly used in the South African mining industry. From the mine responses and discussions with suppliers, it was found that the majority of the mines use two locally manufactured samplers. In addition, two suppliers provided two more samplers which they are promoting to the industry.

Three 25 mm samplers were obtained off-the-shelf for each type of sampler from the respective suppliers. Five samplers were evaluated in this study and these are discussed below.

3.1.1 Aluminium sampler

The aluminium sampler was used as the reference sampler because this sampler is specified in the National Institute of Occupational Safety and Health's (NIOSH) respirable dust methods. The aluminium sampler meets the ACGIH/ISO/CEN respirable criterion that the 50% cut-point is at 4 µm. To meet this criterion the aluminium sampler was operated at a sampling flow rate of 2.5 L/min as specified by the manufacturer.

The aluminium samplers were in good condition, with no physical defects observed. The aluminium sampler was used with a three-piece filter cassette holder.

3.1.2 Sampler ENC

Sampler ENC was a non-corrosive, Higgins-Dewell type sampler (Higgins et al. 1967), manufactured in South Africa. This sampler was operated at 2.2 L/min to yield a 50% cut-point of 4 µm in order to comply with the ACGIH/ISO/CEN convention (Health and Safety Laboratory 1997). This sampler was used in conjunction with the conventional three-piece filter cassette holder.

No defects were found on the ENC samplers.

3.1.3 Sampler SNC

Sampler SNC was a non-corrosive, Higgins-Dewell type sampler (Higgins et al. 1967), also manufactured in South Africa. These samplers were operated at 2.2 L/min to yield a 50% cut-point of 4 µm in order to comply with the ACGIH/ISO/CEN convention. This sampler was also used in conjunction with the conventional three-piece filter cassette holder.

In terms of manufacturing defects, as with the previous study (Pretorius 2010), it was found that there were burrs in the inlets and outlets of the samplers caused by poor finishing during manufacturing. After each run it was apparent that dust had been trapped in these grooves at the inlet.

3.1.4 Sampler C

Sampler C was a Higgins-Dewell plastic sampler which uses centrifugation to remove respirable dust from the airborne dust when operated at 2.2 L/min to obtain a 50% cut-point of 4 µm. Instead of a conventional three-piece cassette this sampler has a customised filter cassette holder with a stainless steel support grid.

No manufacturing defects were found on the cassettes, although with the opening and closing of the cassette holder fine plastic shavings were noticed coming off the cassettes. This could be because the cassettes were still new and the 'grinding' action was shaving off some of the plastic. The concern is that these shavings might end up on the sampled filter and could affect the respirable dust weight.

3.1.5 Sampler SP

Sampler SP was a conductive plastic sampler which also operates at 2.2 L/min to achieve the desired 50% cut-point of 4 µm. Sampler SP is similar to Sampler C in that it also has a customised filter cassette holder with a stainless steel support grid. Sampler SP differs from Sampler C in that the cassette opens up in three parts instead of two.

No defects were found on inspection and smaller amounts of plastic shavings than for C Sampler were noticed coming off the cassettes.

3.2 Sampler Evaluation Methodology

The aerosol dust chamber described in MDHS 101 (Health and Safety Laboratory 2005) for the preparation of calibration standards was used for this study. In accordance with this method, a set of calibration standards was prepared with each of the samplers under investigation.

The test dusts that were used were:

- ISO 12103-1 A3, also known as Arizona medium test dust (0 – 80 µm);
- ISO 12103-1 A1, also known as Arizona ultrafine test dust (1 – 10 µm); and
- NIST 1878a alpha-quartz standard reference material (D_{50} = 1.6 µm).

Arizona dust is often used to test filter and sampler efficiencies and contains a high concentration of crystalline silica (Powder Technology 2008). The National Institute of Standards and Technology (NIST) standard contains 93.7% crystalline quartz (according to the certificate of analysis) and was used to calibrate the XRD for each sampler.

Three samplers of the same type plus an aluminium sampler were placed in the dust-generating chamber at the same time and each connected to its own sampling pump. A weighed amount of dust accurate to 10 μg was placed in the glass bowl of the chamber and made airborne. After 60 seconds all four sampling pumps were started at the same time and switched off after 30 seconds of sampling. The sampling time was the same for all the rounds regardless of the test dust used.

This approach was found to give the most consistent amounts of dust for a given round. The aim was to obtain dust weights on the filter in the region of 0.25, 0.5 and 1 mg Arizona dust respectively.

3.3 Equipment and Instrumentation Used

Calibrated Sensidyne Gillian sampling pumps were used and were operated according to the flow rates specified by the supplier of each sampler.

Mixed cellulose ester (MCE) 25 mm filters were used as the sampling medium. These filters were acclimatised in a weighing room where the temperature and humidity were closely monitored and controlled. The MCE filters were weighed before and after sampling to determine the respirable dust concentration on each filter.

The filters were analysed using an X-ray powder diffractometer (XRD). The filters were placed in a sampler holder on top of a silicon zero-background holder.

A calibration curve was prepared for each type of sampler. Background corrections were made and the peak area was used to calculate the intensity at the three most intense peaks of quartz: 26.64, 20.8 and 50.15 °2θ. Only the results of the most intense peak (26.64 °2θ) were reported in this study.

All five calibration curves were verified using one round of proficiency testing filters from the Workplace Analysis Scheme for Proficiency (WASP) of the Health and Safety Laboratory (HSL) in the UK.

The filters which were sampled with the two types of Arizona dust were then analysed on the XRD. The filters from each sampler type were analysed and quantified using their own calibration curves. The relationship between the gravimetric weight and the XRD response was graphically determined. The data set for each sampler type was analysed using Grubb's test for statistical outliers at the 95% level of confidence.

The PSD was measured with a laser light scattering particle size analyser. The results obtained were multiplied by the square root of the specific gravity of the test dust to obtain the aerodynamic diameter (AED).

4 RESULTS

4.1 Amount of Dust sampled by the Different Samplers

After sampling, the filters were weighed to obtain the amount of respirable dust on each filter. Grubb's test was used to evaluate the gravimetric weights so that any samples which could overly weigh the calibration trend line for each sampler could be removed from the set. No outlying values were found.

Figure 1 gives an indication of the amount of dust collected by the different samplers under the same sampling conditions.

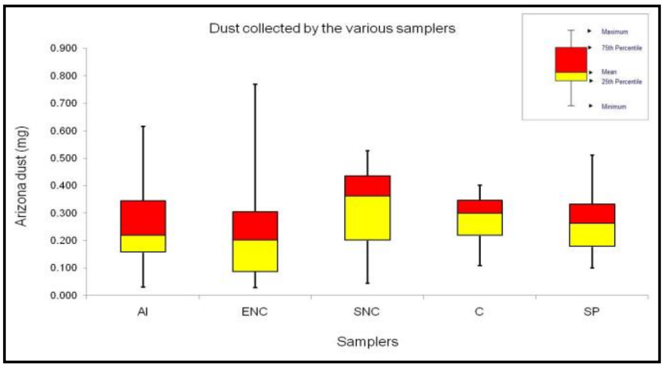

Figure 1: Comparison of the amount of dust collected by each type of sampler

4.2 Calibration Curves prepared for XRD

This section presents the results obtained from the calibrations of each sampler which were prepared with NIST 1878a.

Table 1 gives a summary of the regression lines for each sampler when NIST 1878a was sampled. For all the samplers, more than 93% of the variation in the XRD response can be explained by each sampler's regression formula as described by the coefficient of determination (R^2).

Table 1: Regression line summary for each sampler evaluated

Sampler	**Intercept**	**Slope**	**Regression Coefficient**	**Standard Error of Slope**	**Nr**
Aluminium	-0.325	33.6	0.956	2.008	15
Sampler ENC	-0.340	42.5	0.973	1.753	18
Sampler SNC	-0.661	38.8	0.961	2.162	15
Sampler C	1.067	49.9	0.984	1.779	15
Sampler SP	-0.983	52.7	0.927	4.256	14

All the samplers, apart from Sampler C, have a small negative bias (i.e. a negative non-zero intercept value) associated with their calibration. Sampler C shows a positive bias with an intercept at 1.067. The standard errors on the slopes are quite large and for this reason the intercepts would probably not differ significantly from zero (this observation was not tested).

Chen et al. (2010) found that different samplers gave different uniformities of deposition. The authors found that the more uniform the way in which the dust was deposited on the filter, the lower the quartz concentrations (i.e. XRD response) were for the same amount of dust from the same sampling area. This result could explain why the sensitivities (i.e. slopes) of the calibrations were different even when the same NIST standard was sampled under the same laboratory conditions. This study confirmed the finding by Chen et al. (2010) that the aluminium sampler provided the most uniform dust deposition (i.e. the lowest sensitivity). Sampler SP had the highest slope and would provide the highest sensitivity because the dust is deposited closer to the centre of the filter.

A statistical analysis was performed on the regression results to determine if the regression lines were significantly different from one another. The slope and standard error of the slope were included in the determination of the p-values. Table 2 provides a summary of the p-values for each pair of samplers.

Table 2: Summary of the p-values for each pair of regression lines compared

Sampler	Aluminium	Sampler ENC	Sampler SNC	Sampler C	Sampler SP
Aluminium		0.002	0.095	0.000	0.000
Sampler ENC	0.002		0.193	0.006	0.035
Sampler SNC	0.095	0.193		0.001	0.007
Sampler C	0.000	0.006	0.001		0.549
Sampler SP	0.000	0.035	0.007	0.549	

Where the p-value is less than 0.05 the regression lines from the pair of samplers are significantly different from one another.

The calibration from the aluminium sampler does not differ significantly from Sampler SNC but does differ significantly from the other three samplers. Sampler SNC shows no significant differences when compared to Sampler ENC and the aluminium sampler, but differs significantly from Sampler SP and Sampler C.

The calibration from Sampler ENC was significantly different from all the samplers except for Sampler SNC. Sampler SP and Sampler C were not significantly different from one another. However, when compared to the other three samplers, these samplers were significantly different from all of them.

4.3 Proficiency Testing Results on the Different Calibrations

One round of filters from the WASP scheme was analysed and quantified using all five of the calibrations from the different samplers. The acceptance criterion for the WASP results was that reported values should be ± 10% from the 'true value'.

Table 3: Results for proficiency testing filters when analysed on each of the sampler calibration curves

	SAMPLE 1	SAMPLE 2	SAMPLE 3	SAMPLE 4	AVG	%DIFF
'True Value'	**0.074**	**0.101**	**0.125**	**0.130**	**0.108**	-
Aluminium	0.077	0.112	0.128	0.136	0.114	5.5
Sampler ENC	0.070	0.101	0.124	0.129	0.106	-1.1
Sampler SNC	0.072	0.100	0.125	0.132	0.108	-0.1
Sampler C	0.073	0.103	0.123	0.119	0.105	-2.9
Sampler SP	0.070	0.096	0.115	0.116	0.099	-7.8

Table 3 shows that all the samplers provided quartz results which were within the acceptance criterion range provided by the proficiency testing scheme. The conclusion drawn from these results is that sampler-specific calibrations are necessary to achieve accurate results.

4.4 XRD Response from Arizona Test Dust

This section gives the results obtained from the calibrations of each sampler when Arizona test dust was sampled and analysed. Table 4 provides a summary of the regression lines for each sampler when Arizona test dust was sampled. The tabulated information is based on the combination of the medium and ultrafine dust.

Table 4: Regression line summary for the Arizona test dust sampling

Sampler	Intercept	Slope	Regression Coefficient	Standard Error of Slope	Nr
Aluminium	0.974	6.7	0.410	1.752	23
Sampler ENC	0.943	3.9	0.478	1.144	15
Sampler SNC	-0.087	10.9	0.937	0.709	18
Sampler C	4.624	3.4	0.027	5.289	17
Sampler SP	0.041	18.6	0.867	1.876	17

The regression models for the aluminium sampler, Sampler ENC and Sampler C are not sufficient models to describe the variation in XRD response.

It is only the regression formula of Sampler SNC that describes more than 90% and Sampler C's formula which describes 86% of the variation in XRD response. When these two regressions were compared with one another significant differences were found between the two models.

4.5 Particle Size Distribution (PSD) Results

The PSD was determined from the bulk samples of the test dusts used in this study. The 50% cumulative percentage (i.e. the D50) of the AED for each bulk material was calculated from the measurement as:

- NIST 1878a: D50 = 2.6 µm; D90 = 4.72 µm;
- Arizona ultrafine test dust: D 50 = 5.86 µm; D90 = 14.82 µm;
- Arizona medium test dust: D50 = 24.09 µm; D90 = 79.46 µm.

The D50 and D90 of the AED are reported in Table 5 for each sampler with each test dust.

Table 5: Summary of the AED for each sampler with the test dusts

Sampler	NIST 1878a		Arizona Ultrafine		Arizona Medium	
	D50	D90	D50	D90	D50	D90
Aluminium	1.6	3.2	3.4	55.8*	4.45	6.35
Sampler ENC	1.3	2.9	4.3	6.2	4.28	15.06
Sampler SNC	2.0	3.5	4.4	74.9*	4.91	6.16
Sampler C	2.1	3.1	3.9	6.1	4.74	8.12
Sampler SP	2.5	3.9	2.6	4.1	3.99	4.82

**Possible agglomerates*

When the NIST reference material was sampled to prepare calibration standards, the D50 AED of all the samplers was found to be lower than the supplier-specified 4 µm. The D90 AED values were slightly higher at approximately three micron. Because the NIST dust has a PSD of below 10 µm it is not surprising that the PSDs of all the samplers are below 10 µm.

For the Arizona ultrafine test dust the D50 values were closer to 4 µm for all the samplers apart from Sampler SP. The D90 values were well below 10 µm for Sampler ENC, Sampler C and Sampler SP. The aluminium sampler and Sampler SNC had D90 values of greater than 50 µm. Since the PSD of the bulk material only goes to ~ 20 µm, it is possible that some agglomerates were sampled onto the filter.

The D50 AED values for Arizona medium dust were in the range of 4 to 5 µm and the D90 AED values were well below 10 µm for all the samplers. The only exception was Sampler ENC, which had a small but acceptable percentage of D90 AED above 10 µm.

The performance of samplers in terms of sampling the respirable fraction of dust is critical. If particle sizes of much larger than 10 µm are deposited onto the filters, this could give varying responses from XRD analysis. Not all samplers perform exactly according to the ISO/CEN/ACGIH curve giving a cut-point of 4 µm. The cut-points of samplers may vary according to their design and specifications. But it is expected nevertheless that size-selective samplers sample the respirable portion of airborne dust to determine the exposure of workers to quartz.

5 CONCLUSIONS

From the findings of this study it can be concluded that:

- There is a linear relationship between XRD response and the quartz concentration with the NIST standard reference material for all five of the samplers tested;
- The XRD response is affected by the dust deposition because it determines the sensitivity (i.e. slope) of the calibration;
- Provided that sampler-specific calibrations are used for quantification, it is possible to obtain accurate results within 10% of proficiency testing samples;
- XRD response is affected by the particle size distribution of the dust which is deposited on the filter. If particles larger than the respirable fraction are deposited, a greater XRD response will be obtained (i.e. silica concentration);
- Even though the dust bowl is not ideal for testing samplers with real dust, it is clear that the linear relationship between XRD response and quartz concentration does not hold for real dust.

The performance of size-selective samplers does affect the XRD response during quartz analysis and has an effect on the quartz concentration measured.

6 RECOMMENDATIONS

On the basis of the findings of this project it is recommended that:

- The laboratory analyst should be informed about which sampler was used during the sampling exercise in order to use the appropriate calibration;
- Based on the findings of this study, one sampler could not be recommended for the national standard to ensure that comparable samples are taken across the industry;
- Samplers should be subjected to more stringent quality assurance protocols to ensure

that they perform accurately and consistently with all types of mine ore dust found in the South African mining industry;

- There is currently not one specified method for sampler evaluation and for this reason a quality assurance protocol needs to be developed. The aerodynamics of the sampler should be evaluated in addition to factors such as the actual dust deposition on the filter, PSD of the sampled dust and the effect of the sampler performance on the quartz concentration when measured using direct-on-filter XRD; and
- The performance of samplers should be evaluated in the real (underground) mining environment.

REFERENCES

Chen, C-H, Tsaia, P-J, Lai, C-Y, Penga, Y-L, Soo, J-C, Chen, C-Y and Shih, T-S. 2010. Effects of uniformities of deposition of respirable particles on filters on determining their quartz contents by using the direct-on-filter X-ray diffraction (DOF XRD) method. *Journal of Hazardous Materials*, 176: 389–394

Health and Safety Laboratory. 1997. Customer Report (Job C510008.97).

Health and Safety Laboratory. 2005. MDHS 101. *Direct-on-filter analysis by infrared spectroscopy and X-ray diffraction*. *Methods for the determination of hazardous substances* (February 2005).

Higgins, R.J. & Dewell, P. 1967. A gravimetric size selecting personal dust sampler. In C.N. Davies (ed.), *Inhaled particles and vapors II:* 575-586. Oxford: Pergamon Press.

International Organization for Standardization (ISO) 2009. Workplace air: Guidance for the measurement of respirable crystalline silica. Geneva, Switzerland: International Organization for Standardization, ISO 24095.

Powder Technology. 2008. *Material safety data sheet of Arizona dust*, www.powdertechnologyinc.com/msds/01msdsArizona TestDust010908.doc

Pretorius, C.J. 2010. Particle-capturing performance of South African non-corrosive samplers. In Mine Ventilation Society (MVS) Conference: The responsibilities and functionality towards ventilation control in mines, Emperor's Palace, 13-14 May 2010.

SKC. The use of aluminium cyclones, SKC Technical Note, Publication 1519, Rev 1103.