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EVALUATION OF PERFORMANCE CHARACTERISTIC BETWEEN DIRECT AND INDIRECT SAMPLING METHOD FOR RESPIRABLE CRYSTALINE SILICA (RCS) EXPOSURE IN GRANITE QUARRY

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ABSTRACT

Selecting the best sampling method for respirable crystalline silica (RCS) exposure always is a debate among industrial hygienist. The dispute is always focusing on the diversity between direct and indirect method which may contribute to uncertainty in final result. The objective of this research is to define applicability of direct and indirect method in determination of RCS exposure in Malaysia. Beside, this study aims to determine the best method in terms of performance characteristic. Parallel 8 H exposure sampling was performed among 30 workers at 6 granite quarries located in Selangor and Kuala Lumpur, Malaysia. Based on overall measurement uncertainty value, we determine that indirect method has better performance characteristic compared with direct method. However, inferential statistic by Spearman's rank order correlation test indicate significant positive correlation ($r(30)=0.427$; $p<0.05$), and different test Wilcoxon sign rank test, showed no significant difference between bot set of data. These indicate that there is no significant difference on exposure data between both methods.

Keywords: quartz, NMAM 7500, MDHS 101, granite, quarry.

1. INTRODUCTION

Exposure to RCS in granite quarry posed significant risk to silicosis and lung cancer among workers. In Malaysia, RCS exposure in quarry industries is not well established due to constraint in local capabilities to perform specific monitoring on RCS.

There is several monitoring method for RCS published by established authorities or agency all over the world. In the United State of America, method for RCS sampling was published by National Institute of Occupational Safety and Health (NIOSH), Occupational Safety and Health Administrator (OSHA) and Mine Safety and Health Association (MSHA). The method are NIOSH Manual Analytical Method No.7500 (NMAM 7500) which is Silica, crystalline, by X-ray Difractometer via Filter Deposition[1]; NIOSH Manual Analytical Method No.7602 (NMAM 7602) which is Silica, Crystalline by Infrared (KBr pellet)[2]; OSHA ID 142 which is Quartz And Cristobalite In Workplace Atmospheres[3]. and MSHA P2 which is X-ray Diffraction Determination of Quartz and Crystobalite In respirable Mine Dust[4]. In United Kingdom, Health Safety Laboratory established a RCS method namely Methods for the Determination of Hazardous Substance Guidance No.101 (MDHS 101) which is Respirable Crystalline Silica in Respirable Airborne Dust)[5]

In general monitoring method for RCS may be divided to direct method and indirect method. Direct and indirect methods are often in competition in industrial hygiene to measure the airborne concentration of a pollutant in workplaces[6]. The dispute is always focusing on the different technique used for sample preparation which may cause error in final result. Direct method means that field sample will be directly analysed without any pre-treatment procedure. Indirect method means that field sample will undergo a series of pre-treatment involving digestion, filtration or ashing process. Even though sampling technique among direct and indirect methods are similar but the analytical procedures are apparently different among them.

Selection of method will much depend on resource such as sampling equipment, skill and laboratory capabilities. It is common that different laboratory will offer different analytical method based on their instrumentation availability. Employer and industrial hygienist are free to choose any method that is offered by the laboratory. Often selection will be based on methods performance characteristic and quality assurance data showed by the laboratory. The purpose of quality assurance program in industrial hygiene analytical procedure is to ensure the reliability of reported data[7]. In other way good quality assurance will ensure that the results are reliable and meeting objectives of sampling. In general, performance characteristic for a method development and validation will much depend on the accuracy of test which include precision and trueness evaluation. Besides that, validation also include applicability, selectivity, calibration linearity, range, detection limit, ruggedness, fitness for purposed, matrix variation and measurement uncertainty [8, 9]

2. OBJECTIVES

The objective of this research is to compare applicability of RCS sampling and analysis between direct and indirect method using X-ray diffraction technique. Beside that, this study aims to determine the best method in terms of performance characteristic.

3. METHODOLOGY

Sampling and analytical method strictly followed MDHS 101[5] which represent direct method and NMAM 7500[1] which represent indirect method. Both methods apply X-ray diffraction (XRD) technique for analysis. Sampling was performed at 6 quarries located in Kuala Lumpur and Selangor. The area was selected due to highest production of granite in Malaysia. 5 to 7 workers were selected from each quarry. These workers are crushing operators and are considered to have similar exposure.

Sampling was performed throughout their 8 hours work shift period. Each worker was supplied with two sets of integrated sampling set. All samples were collected in pair to create parallel set for comparison for direct and indirect method. Each set consist of standard flow SKC sampler, attached with SKC GS3 cyclone and 2 pieces cassette loaded with 5.0um of Poly vinyl chloride (PVC) filter. We used SKC GS3 respirable cyclone as separating device for respirable fraction. We apply flow rate of 2.75 L/min as specified by manufacture. Flow rate of 2.75 L/min are proposed by manufacturer to meet 4.0 µm 50% cut of point of respirable fraction[10]. The specification pattern are similar with respirable convention definition [10].

Laboratory procedure starts with generation of standard range filters from bulk standard. For the purposed of this research, we used JAWE 461[11] supplied by Japan Association for Working Environment Measurement (JAWE). The purity of quartz is 99.32%. Calibration curve was established by comparing the known weight of the quartz on the filters as against the intensity response of the X-ray diffraction. In direct method, standard filter was generated in a polycarbonate chamber. Different range of standard weight filters cassette was generated by adjusting the pump running time. In indirect method, standard filter was generated from vacuum filtration assembly system. Four standard ranges of 50µg/L, 100µg/L, 250µg/L and 250µg/L were produced. Each standard was filtered on 25mm silver membrane via vacuum filtration system. Both set of calibration standards was analysed by XRD analysis.

Two series of laboratory validation data were derived of each direct and indirect method. Detection limit was established from 10 replication of the lowest standard range. Each article was prepared and analysed independently. Limit of detection (LOD) was established by multiply standard deviation (SD) value with three. Limit of quantification (LOQ) was established by multiply SD value of 10. Accuracy data were established from precision and trueness data. Data was established by preparing 10-20 known value of spike filter samples generated from JAWE 461 and by readymade filter from of standard reference material (SRM) 2950; respirable alpha quartz on filter media, purchased from JAWE. The SRM 2950 was purchased from National Institute of Standard and Technology (NIST) of United States of America. SRM 2950 consist of 25mm PVC filters containing known mass of 10 µg, 20 µg, 50 µg, 100 µg, 250µg and 500µg respirable quartz with uncertainty value between 4.9% to 11.5% of the weight[12].

In the final stage, parallel samples from quarries were analysed. In total, 30 sets of personal and six area samples were collected to represents both direct and indirect. For direct method, filters were analysed by X-ray diffraction without any pre-treatment procedures. Direct method use 25mm PVC filter, the filters can be directly placed into 25mm samples holder of XRD auto sampler. 37mm PVC filters from indirect method will require filter treatment procedure to convert samples from 37mm filter to 25mm filter to make it fit with XRD auto sampler. Analyses of indirect method involving acid treated with 10ml of 25% hydrochloric acid and 5 ml of 2-propanol and heated in muffle furnace for 2 hours at 600`C. The ash will be dissolve in 15 ml 2-propanol filters on silver filter by vacuum filtration process. Filtration process will initiate homogenous layer of quartz dust on filter surface.

Measurements of quartz were performed by XRD, Rigaku model Multiflex equipped with six holder auto samplers with sample spinner. An X-ray generator was used to obtain maximum output of 2000 Watt (tube voltage 40kV; tube current 50mA). Scanning range of primary peak of quartz at range 26˚to 27.14˚. Results were obtained from integral intensity of the signals.

Table-1. Differences on sampling and analytical technique between direct and indirect method.

	Direct Method	Indirect Method
Reference method	MDHS 101	NMAM 7500
Method Published by	HSL, HSE, UK	NIOSH USA
Filter type	25 mm PVC filter	37mm PVC filter
Standard preparation by	By exposure chamber	By funnel filtration system
Sample preparation by	Direct filter method (no treatment)	Digestion with acid and ashing

4. RESULTS AND DISCUSSION

4.1. Method performance characteristics

Table-2 and 3 explains the comparison data for methods performance characteristic between direct and indirect method. In general, performance characteristic for method development and validation will much depend on the accuracy studies which include precision and trueness. Besides that, validation also include applicability, selectivity, calibration linearity, range, detection limit, ruggedness, fitness for purposed, matrix variation and measurement uncertainty.

Table-2. Method performance characteristic between direct and indirect methods.

Performance Characteristic	Unit	Direct method	Indirect method
Calibration range	µg	17.33-570	10-500
Calibration regression	-	0.996	0.999
Limit of detection (LOD)	µg	13.04	4.11
Limit of quantification (LOQ)	µg	43.46	13.70
Trueness- recovery (%)	%	95.6	90.7
Precision-standard uncertainty reproducibility (pooled RSD)	%	5.44	3.92
Total combined standard uncertainty	%	12.51	10.54

Table-3. Method performance characteristic for trueness and precision between direct and indirect methods.

Test	Direct Method			Indirect Method		
	Reproducibility		recovery	Reproducibility		recovery
	mean	SD		mean	SD	
1	216.1	2.2	90.7	85.73	1.9	85.7
2	261.6	7.14	104.6	219.5	13.3	87.7
3	91.56	6.72	91.6	98.61	1.19	98.6
	Pool RSD: 5.4%		95.6%	Pool RSD: 3.9%		90.7%

LOD study always performed at lowest possible concentration [13]. By this reason LOD for indirect method was performed at the lowest of calibration point at 10µg. However for direct method, MDHS 101 suggested that linear relationship between diffracted intensity and mass may not hold at very low concentration[5]. This is mean that extrapolation straight line does not usually pass through the origin and contribute to uncertainty in the LOD. Due to this factor, LOD for direct method was performed at higher calibration point at approximately 100ug.

In general worldwide stipulated permissible exposure limits (PELs) for respirable quartz are very low levels which are between 0.05 and 0.1 mg/m^3. In this situation, it is very important for laboratory to establish LOD at very low range to ensure that assessment can be determine at very low level of PEL and provide confident on compliance status. LOD should be at least less than 10% of PEL. In this research, we identified that the LOD for indirect method are lower than direct method. LOD of direct method is at about 30% of PEL while for indirect method is about 10% of PEL. Estimation is based on minimum volume of samples required by each method. Most procedures are reporting method detection limit values of 3-5 µg which is within 10% of the PEL[14].

Both methods showed calibration regression at more than 0.99. Calibration slope are different between these two methods. These conditions indicate that the samples and calibration must be prepared at same manner. Cross examination of samples and calibration set between these two methods will cause major systematic error to final result.

After many batch of analysis, we find out that calibration filters for indirect method is more stable compare with indirect method. In direct method, dusts are deposited on the calibration filter via quartz cloud generation. This method cannot ensure homogenous separation of the dust on the filters and these contribute to instability of the calibration curve.

Total Recovery for direct method is about 95.6% while recovery for indirect method is 90.7%. Both values are still within acceptable range as per Association of Analytical Communities (AOAC), Official Method of Analysis Guidelines for Standard Method Performance Requirements[15]. Ashing process might reduce a small fraction of quartz and lead to negative recovery of the data[6]. Study conducted by Page, S.J in 2006 indicates that indirect method (NMAM 7500) is likely to underestimate content of RCS within 5-10% while another study performed by Kauffer et al estimated bias at about 5-7%[6]. He also indicate that XRD could underestimate the silica content as much as 8.5% if the respirable aerodynamic equivalent diameter (AED) is less 3.6 µm[16]. Considering that this research only cover respirable fraction with AED less than 10µm, reduction of recover might be caused by higher percentage of very small AED particles.

Indirect method showed better precision compare with direct method. Table-3 show that pooled relative standard deviation (RSD) of direct method is at 5.4% while for indirect method is at 3.9%. In indirect method calibration and samples filters are suspended and homogenised in propanol or tetrahydrofuran and filtered on a silver membrane. These processes facilitate homogenised particle separation on the filters and reduce deviation on XRD analysis. However, in direct method, since there is no pre-treatment of the calibration and samples filters, the RCS particles are not homogenised and cause higher variation on the XRD analysis. Findings indicate that direct method showed better recovery at 95.6% compared with indirect method at 90.7%. These mean that direct method is less bias and closer to the true value compared with indirect method. In overall of uncertainty estimation of both methods, indirect method showed better uncertainty values at 10.54% compare with direct method at 12.51%.

4.2. Comparison of field samples between direct and indirect method

30 parallel eight hours personal samples were collected from six quarries. The workers are crusher operators and are considered to be similar exposure group. Both methods were sampled in same setting except for filter size. Direct method use 25mm PVC filters while indirect method used 37mm PVC filters.

Table-4. Comparison on personal exposure between direct and indirect method.

Method	n	Mean (mg/m^3)	Range (mg/m^3)	Above PEL
Direct method	30	0.11	0.02-0.41	40.0%
Indirect method	30	0.091	0.02-0.26	36.7%

Spearman rank order correlation test was chosen for correlation between exposure data of direct and indirect methods. Result from Spearman's rank order correlation test indicate significant positive correlation (r (34)=0.427; $p<0.05$). We can agree that high results in direct method are associate with high result in indirect method.

Wilcoxon sign rank test was chosen to identify differences of personal exposure data between direct and indirect method. Based on Wilcoxon sign rank test, distribution of the exposure data between direct and indirect method showed no significant difference with, z=-1.419, $p>0.05$ respectively. This indicates that there is no significant difference on exposure data between both methods.

Table-4 indicate descriptive data based on eight hour time weighted average (8H TWA) personal exposure of RCS among crusher operators. Mean of personal exposure for direct method is 0.11 mg/m^3 while mean for indirect method is 0.091 mg/m^3. Lower mean result in indirect method is consistent with lower recovery as mention in Table-2 and 3. Even though samplings were performed in parallel in same setting, workers exposure may slightly differ due to wind direction and workers movement position. Based on evaluation on both data, direct method showed 40.0% of sampled workers are exposed above the Malaysia's permissible exposure limit (PEL) while indirect method showed lower value at 36.7%. The PEL comparison is based on Occupational Safety and Health (Use and Standard of Exposure Chemical Hazardous to Health) Regulation 2000.

5. RECOMMENDATIONS

There are few issues that need to address and recommended to industrial hygienist while selecting sampling and analytical method for RCS exposure and Industrial hygienist may apply any of both methods base on their preferences

In term of overall performance characteristic, based on overall uncertainty value, we can determine that indirect method has better performance characteristic compared with direct method. Beside that indirect method is more precise, and has better detection limit. Beside that its calibration standard is more stable and can be reused for longer time than direct method. Furthermore NMAM 7500 is fully validated and the only method with any legal significant[17]. But Analysis of indirect method is more expensive due to additional proses on sample preparation especially on high cost for silver filter membrane

Direct method procedure produce less stable calibration curve, but this calibration filter mimic actual field samples initiate less systematic error to final result. Beside, direct method produces better recovery compared with indirect method.

Despite the differences between performance characteristic and actual field sampling result, both direct and indirect method meet acceptable range as per Association of Analytical Communities (AOAC), Official Method of Analysis Guidelines for Standard Method Performance Requirements[15]. Beside that statistical analysis showed that there are no significant differences between both set of field data.

6. CONCLUSIONS

Based on performance characteristic between both data we conclude that indirect method showed better performance characteristic. However, statistical analysis on actual field samples showed that there is no significant different between results on both methods.

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