Application of X -ray Diffractometry on Analysis Crystalline Free Silica in Foundries

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Abstract

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To assess the concentration of crystalline free silica, which the workers in the operating environment were exposed to, personal sampling equipment is mainly used for respiratory dust and total dust collection. In the research, we found that the uniformity of surface samples would affect the XRD analysis of up to 50% error. The Central Cyclone opened cartridge could obtain uniform surface analysis using the Japanese JIS A1481 X -ray diffraction analysis method with the base standard absorption correction. In addition, we could even obtain a better linear relationship under low concentration.

As for the exposure status in the foundry industry operations at the scene investigating crystalline free silica, we analyzed the samples collected from the foundry industry: pouring, shakeout and deburring, and then explored the crystalline free silica exposure in foundries. The results showed a good correction coefficient for aluminum crystalline free silica. In the operating environment, there was ND-7.75% (ND-0.07 mg/m^3) of respiratory crystalline free silica content; the total dust in play sand with higher levels of operational area was 1.72-29.31% (0.07-2.06 mg/m^3). This method is simple, environmentally friendly, low-cost, and has characteristics of non-destructive analysis, so we hope it can provide efficient concentration investigation about industry exposure, and thus improve the working environment and ensure the health of workers.

Keywords: Foundry, Crystalline free silica, Uniformity, χ -ray diffractometry

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Preface

The crust is mainly constructed from the elements of iron, magnesium, silicon, and oxygen, and the silicates mainly constructed of silicon and oxygen can be seen in geology. The silicates are combined by silicon, oxygen atoms, and other elements; it is also called combined silica. In which, the crystalline free silica refers to that the silicon and oxygen atoms follow certain characteristics in the arrangement of crystals. The distance between each atom is the same, and has a certain crystallization shape. The most common crystalline free silica is quartz, cristobaltie and tridymite. Crystalline free silica has tolerance and special shape variability for high-temperature, and therefore it is widely used in industrial processes, such as the brick industry, and foundries. At the same time, it may, due to different special industrial processes, have the high-risk of exposing crystalline free silica, such as: in foundries, the tunneling industry, incinerator furnace demolition work, and the air ceramics industry.

Foundries can be called the mother of industry; they were used in the manufacturing of weapons in the early years, and widely used in the manufacturing of machine tools and machine parts after industrialization. Currently there are 407 legally registered metal foundries in Taiwan, and 13,922 employees. (1) Due to the casting process being very cumbersome, the exposed harmful factors also vary, such as the exposure of crystalline free silica, mineral fibers, high-temperature metal fumes, ionizing and non-ionizing radiation, and noise and vibration. It was found in past studies that when foundry workers are exposed to fresh crystalline free silica for more than 20 years, their chance of having Pneumoconiosis will increase. (2) In recent years, the domestic occupational Pneumoconiosis payment is about 10%. (3) In the recent 5 years, 11 workers have been diagnosed with Pneumoconiosis and related complications.

According to literature, the harm of crystalline free silica to the human body includes Pneumoconiosis (silicosis) (4) Lung cancer (5) Infectious lung diseases (6) Abnormalities in pulmonary function (7, 8) Autoimmune disease (9, 10) Corpulmonale (9, 10) and Nnephritis. Therefore, the International Agency for Research on Cancer (IARC) listed crystalline free silica as a “human carcinogen” in 1997. (5) The world has listed crystalline free silica as a workplace hazardous material.

Currently, the domestic crystalline free silica allowable concentration standard is mainly divided into more than 10% and less than 10%. The allowable concentration of breathable dust for more than 10% crystalline free silica concentration is 10 $mg/m^3/(\%SiO_2+2)$; the total dust is 30 $mg/m^3/(\%SiO_2+2)$. The allowable concentration of breathable dust for less than 10%

crystalline free silica concentration is 1mg/m^3; the total dust is 4 mg/m^3. The allowable concentration calculation formula is used by Taiwan, India and the Occupational Safety and Health Administration, U.S.A. (OSHA), and other countries all apply a single value for allowable concentration control. For example the American Conference of Governmental Industrial Hygienists (ACGIH) recommends setting the allowable concentration as 0.025 mg/m^3, the National Institute for Occupational Safety and Health (NIOSH) sets it as 0.05 mg/m^3, and The Japanese Society for Occupational Health (JSOH) sets it as 0.03 mg/m^3. Currently, Taiwan cannot accurately point out the crystalline free silica concentration percentage in the analysis method for workplace air environment. The current status calculated with 90-100% of the base purity, which has resulted in an overestimation of exposed concentration in the workplace. Therefore, how to obtain an accurate crystalline free silica concentration percentage in the workplace dust and the actual exposed concentration of workers are the most important issues for the study.

The most commonly used crystalline free silica analysis method in the world includes (11) infrared spectroscopy (12) and the χ-ray diffraction method (13). Due to the pre-treatment of spectrophotometry requiring at least two days, and that at the same time the accuracy and precision are poorer than the infrared spectroscopy and χ-ray diffraction method, and it cannot distinguish the isomers and requires a large amount of solvent to remove the impurities. Therefore, it is not common to use spectrophotometry. Compared with spectrophotometry, the pre-treatment time of infrared spectroscopy is significantly reduced, however it still needs to use a large amount of organic solvent to remove the impurities, and personal proficiency will create a tremendous difference. Therefore, the accuracy and precision are not as good as the χ-ray diffraction method. The χ-ray diffraction method can mainly be divided into the U.S. NIOSH 7500 and Japan JIS A1481. The major difference between the two methods is whether a silver membrane is used or not. NIOSH 7500 uses a silver membrane as the substrate of the base background correction, however the silver membrane is expensive, and at the same time will have great variability due to different factory batches. JIS A1481 is the sample collected by filters. It does not need pre-treatment and it uses the analysis sample plate (zinc or aluminum) directly as the substrate of the base background correction. Therefore, the Japan JIS A1481 χ-ray diffraction method is used as the analysis method for crystalline free silica.

As such, the study selected the foundry as the study object, applied the Japan JIS A1481 χ-ray diffraction

method as the analysis method of crystalline free silica, and expects to obtain the crystalline free silica concentration percentage and actual exposure status of the foundry's workplace air environment.

Material and Method

1. Study object selection

In Taiwan's iron and steel foundries, the registered iron and steel foundries of the Council of Labor Affairs are selected, and the field sampling of different operation patterns are processed. The dust hazards of iron and steel foundries are mainly the manufacturing of sand molds, sand removal, sand blasting and edge brushing. As foundry space is limited, many processing spaces are repeated, and there is no clear segmentation. Therefore, the sampling location selection is mainly based on the operation type at the sampling time.

2. The analysis of the base standard absorption correction method

Base standard absorption correction explores the impact of sample concentration on intensity. It does a correction comparison on the base standard material before sampling with different back off intensities to calculate the concentration of crystalline free silica; the method is applicable to quartz, cristobaltie and tridymite. It is proposed to use zinc plate or aluminum plate, however as the study requires a consistent base to process sample correction, the study used the same blank filter, and processed individual testing on the zinc plate and aluminum plate, and then brought the blank filter to the workplace for air dust sample collection. After returning to the lab, it respectively processed analysis of the zinc plate and aluminum plate, and input the result into the software for analysis calculation to obtain the correction coefficient (K_f) and further explore which plate has a more stable analysis result on crystalline free silica.

3. Workplace air sampling cyclone

The study's respirable dust sampling applies SKC 25mm aluminum cyclone (2.5L/min) (SKC Inc. U.S.A.) and GS-3 cyclone (2.75L/min) (SKC Inc. U.S.A.), which respectively uses the 25mm PTFE coated glass fiber filter (T60A20) (Pall Life Science, U.S.A.) for workplace respirable dust sample collection. In addition, the total dust sampling applies the SIBATA (Tokyo, Japan) total dust sampler (2.0L/min) which also uses the 25mm PTFE coated glass fiber filter for workplace total dust sampling.

4. Sampling preparation

Before sampling, the 25mm PTFE coated glass fiber filter must be placed in constant humidity incubator overnight. Then remove the filter and use a five-digit electronic weighing scale to record it weight, and then place it in the sampling filter cartridge and seal it to avoid contamination. Respirable dust

sampling: Place the 25mm PTFE coated glass fiber filter in the opened sampling cartridge, seal the sampling filter cartridge with the sampling cartridge seal, place on the cyclone, and use the filter cartridge base to fix the filter cartridge and cyclone together. Total dust sampling: place the 25mm PTFE coated glass fiber filter in the opened sampling cartridge.

Place the sampling equipment and process the on-site correction and record of the sampling pump upon arrival at the workplace. The two ends of the sampler are respectively connected to the respirable sampler and high-flow personal sampling pump for 6-hours of sampling, and at the same time measure and record the workplace temperature and humidity. After the sampling is done, reconfirm the flow rate of the sampling pump, then remove the filter cartridge, seal the filter cartridge opening, and bring it back to the lab and place it in the humidity incubator overnight for weighing and analysis.

5. Sampler's uniformity test

Filter uniformity will impact the χ-Ray Diffractometer (XRD)'s accuracy on quantitative crystalline free silica. The study respectively copes with the opened cartridge and closed cartridge filter cartridge, and then with the stage 1 to 3 medium rings, processes sampling with a flow rate of 2.5 L/min and 2.75 L/min; the collected samples will be analyzed with XRF (Kyoto, Japan). The center of the filter is the origin. The samples' composition is analyzed every 1mm from the right and left of the origin to explore the samples' uniformity of the filter.

6. Machine analysis condition

The χ-Ray Diffractometer used by the study is the Shimadzu XRD-6000 (Kyoto, Japan), the monochromator is graphite monochromator, the copper is an emission source, the applied energy is 40 kV-30mA, and the slit setting is DS:1°;SS:1°:RS:0.3mm. The sample scanning speed is 0.5°/min, the rotating plate rotates the samples at a speed of 30 rpm to obtain the best sample uniformity, and it copes with the cooling system to control the XRD system temperature at 23±2C°. In addition, the configuration method of calibration curve concentration (0.03mg-2.49mg) uses standard material to process the dust recurrence method to collect the same amount of the respirable dust and total dust.

Result

1. The correction coefficient comparison result of the base standard absorption correction method

The study uses the same blank filter to respectively process analysis on the zinc plate and aluminum plate, and obtain the correction coefficient (K_f). The result shows that there are 6 tested samples in this part, the correction coefficient of the aluminum plate is

between 1.0881 and 1.3592, and the correction coefficient of the zinc plate is between 0.8390 and 0.9334. As the major purpose of the base standard absorption correction method is to correct the reduced intensity of the diffracted low concentration samples, Table 1 shows that after the correction, the aluminum plate has better results. The calibration curve concentration linear relationship r=0.995 and above, which has repeated the better result of the repeatability test, cv%=2.84% (n=7), LOQ: 0.02mg. Therefore, the study selected the aluminum plate as the standard absorption correction element for the crystalline free silica analysis plate.

2. The impact of filter uniformity on XRD intensity

Prepare an isopropanol solution that contains 1% quartz, and titrate with the same amount but of different uniformity on the filter, as shown in Figure 1, to process the testing of the impact of filter uniformity on XRD. The result shows that the intensity of more concentrated samples will be 1.5 times higher than the evenly spread samples. The intensity of samples concentrated in the filter center will be 2 times higher than the evenly spread samples, as shown in Table 2. It means that in sampling, if the dust is non-homogeneously concentrated on the filter (closed cartridge), the XRD will be overestimated.

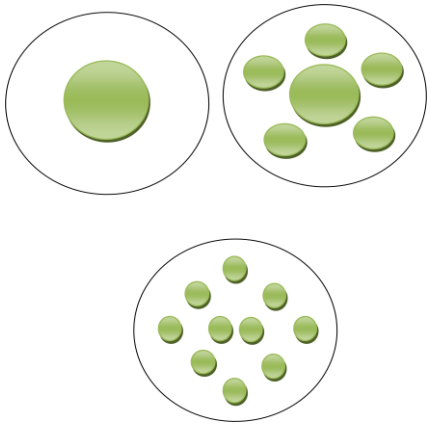

Figure 1. Filter uniformity test diagram

3. Sampler allocation

Sampler allocation will have an impact on filter uniformity; it can be known from the aforementioned result that the allocation test of the closed cartridge sampler may have a 50% impact. Therefore, the study focused on foundry operation again for actual sampling. As in the foundry samples, the content of sulfur and iron are also very high. The samples use XRF to process component concentration analysis. Apply aluminum cyclone to cope with different sampling filter cartridges; the result shows the dust of the stage 1 medium ring coping with closed cartridge sampling concentrated in the center of the filter, as shown in Figure 2 (Y: Intensity (cps), X:mm), the dust of the stage 2 medium ring coping with closed cartridge sampling also concentrated in the center of the filter, and only the dust of the stage 3 medium ring coping with closed cartridge sampling is more evenly distributed on the filter. However, the sampler

allocation is too long, which is difficult to apply during actual sampling. The stage 1 medium ring coping with opened cartridge sampling presents good uniformity (Figure 3). In addition, the GS-3 cyclone and aluminum cyclone are also used to process the same test; the GS-3 cyclone has poorer filter uniformity than the aluminum cyclone, shown as Figure 4.

Table 1. Aluminum plate, zinc plate correction coefficient comparison table

	Intensity (cps)	Correction coefficient (K_f)	Intensity after correction
	Aluminum plate		
A	3987	1.0881	4338
B	5869	1.2615	7404
C	8441	1.2560	10602
D	26550	1.2578	33396
E	41522	1.3011	54024
F	62260	1.3592	84624
	Zinc plate		
A	2272	0.8390	1906
B	5662	0.8408	4760
C	9969	0.8435	8409
D	23201	0.8391	19467
E	40677	0.8879	36117
F	62360	0.9334	58198

Table 2. The impact of filter uniformity pm XRD intensity

Sample characteristic description	Intensity (cps)
Titrate 1 drop of 50μL 1% isopropanol solution that concentrates in the center of the filter	31951
Titrate 1 drop of 25μL 1% isopropanol solution that concentrates in the center of the filter, and 5 drops of 5μL isopropanol solution that are evenly distributed on the filter	24287
Titrate 10 drops of 5μL 1% isopropanol solution that are evenly distributed on the filter	15734

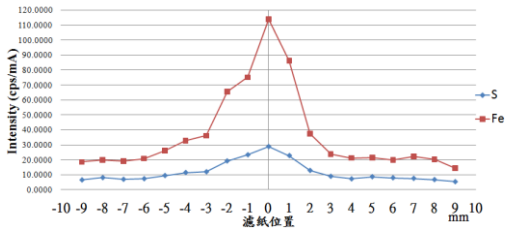

Figure 2. The filter uniformity distribution for the stage 1 closed cartridge aluminum cyclone

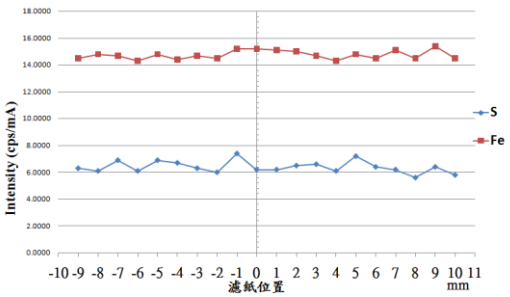

Figure 3. The filter uniformity distribution for the stage 1 opened cartridge aluminum cyclone

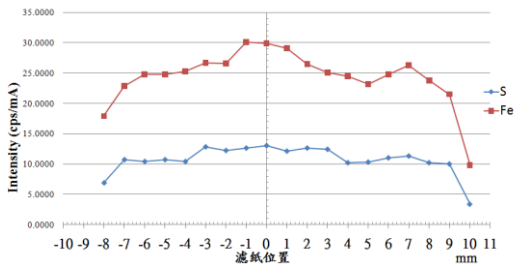

Figure 4. The filter uniformity distribution for the stage 3 GS-3 cyclone

4. Workplace crystalline free silica concentration distribution result

According to the aforementioned pre-test, the study applied aluminum cyclone coping with the opened cartridge stage 1 sampling cartridge, and the SIBATA opened sampler to process foundry workplace sampling. Tables 3 and 4 show that the amount of crystalline free silica will be impacted by different operational type foundries and casting sizes. Generally speaking, the crystalline free silica content of respirable dust is mostly in the lower limit of the calibration line, a small part of crystalline free silica content can be tested to be less than 10%. The crystalline free silica content of the total dust is between 10% and 30%. The crystalline free silica content of different foundries will be different due to the operational types and casting differences.

The crystalline free silica content of Foundry A during the mold releasing: the crystalline free silica content of the total dust is between 11% and 30%. After inputting the value in the domestic workplace air allowable concentration standard formula, the different operational location of the workplace can be divided into the sand removal shaker area, sand removal shaker boundary, and sand blasting area; the concentration is respectively 0.60 mg/m^3, 0.08 mg/m^3, and 2.06 mg/m^3. The result shows that the sand blasting area is the one that is more than the PEL-TWA value. In addition, this foundry's casting is large-size casting, so therefore the respirable dust collected in the edge brushing processing area contains 1.00~7.75% crystalline free silica. No crystalline free silica content is detected in the respirable dust, and the crystalline free silica content in the total dust is about 20% during the Foundry's casting operation. Different operation areas can be divided into the furnace area and casting areas 1 and 2. The air concentration is 0.93 mg/m^3, 0.92 mg/m^3, and 1.05 mg/m^3, as shown in Table 3.

The crystalline free silica content of Foundry B during the mold releasing: the Foundry will humidify the workplace before mold releasing, so no crystalline free silica content is detected in the respirable dust during the mold releasing, and the crystalline free silica content in the total dust is about 8% and 16%. Different operation areas can be divided into the mold removal area, sand blaster area, and general boundary. The concentration distribution is 0.07 mg/m^3, 0.27 mg/m^3, and 0.11 mg/m^3. No

crystalline free silica content is detected in the respirable dust during the casting operation. However, the crystalline free silica content in the total dust is about 10%. Different operation areas can be divided into casting areas 1, 2 and 3, and the concentration distribution is 0.07 mg/m^3, 0.50 mg/m^3, and 0.11 mg/m^3. No crystalline free silica content is detected in the furnace area, as shown in Table 4.

Table 3. Foundry A's crystalline free silica expose concentration

Location	SiO_2 content percentage (%)	SiO_2 dust concentration (mg/m^3)	regulation allowable concentration (mg/m^3)	Note
mold releasing				
Sand removal shaker	14.55	0.60	1.81	T
	N.D.	N.D.	1.00	R
Shaker boundary	11.68	0.08	2.19	T
	N.D.	N.D.	1.00	R
Sand blaster	29.31	2.06	0.96	T
	1.00	N.D.	1.00	R
Edge blushing processing area	2.18	0.02	1.00	R
	7.75	0.07	1.00	R
Casting operation				
Furnace area	19.92	0.93	1.37	T
	N.D.	N.D.	1.00	R
Casting area 1	20.57	0.92	1.33	T
	N.D.	N.D.	1.00	R
Casting area 2	22.16	1.05	1.24	T
	N.D.	N.D.	1.00	R

Note: N.D. is non-detect; T is total dust; R is respirable dust

Discussion

As aluminum plate has better intensity correction for crystalline free silica, the zinc plate cannot correct the reduced intensity due to diffraction, therefore, the study selected aluminum plate as the base of base standard absorption correction method.

Due to there are many commercial respirable samplers, and the basic requirement for XRD test is the filter sampling uniformity, if the sample uniformity is poor, it will result in great error in the XRD quantitative analysis; in addition, In addition, installing a rotating plate on the analysis sampler will allow the filter to be evenly scanned to obtain better repeatability. The reason for past studies not being able to obtain good sample uniformity is using closed cartridge filter cartridge, as the dust will enter the filter cartridge from the cyclone, the closed cartridge filter cartridge has limited the dust to enter the filter, and result in a fluid line causing the sample to concentrate in the center of the filter, and finally obtain poor sample uniformity and result in great error of analysis.

Table 4. Foundry B's crystalline free silica expose concentration

Location	SiO_2 content percentage	SiO_2 dust concentration	regulation allowable	Note

	(%)	(mg/m^3)	concentration (mg/m^3)	
mold releasing				
Mold removal area boundary	8.05	0.07	4.00	T
	N.D.	N.D.	1.00	R
Mold removal area boundary	10.85	0.07	2.33	T
	N.D.	N.D.	1.00	R
Sand blaster	16.08	0.27	1.66	T
	N.D.	N.D.	1.00	R
Boundary environment	11.98	0.11	2.15	T
	N.D.	N.D.	1.00	R
Casting operation				
Furnace area	N.D.	N.D.	1.00	R
Casting area 1	1.72	0.07	4.00	T
	N.D.	N.D.	1.00	R
Casting area 2	9.23	0.50	4.00	T
	N.D.	N.D.	1.00	R
Casting area 3	4.93	0.11	4.00	T
	N.D.	N.D.	1.00	R

Note: N.D is .non-detect; T is total dust; R is respirable dust

The crystalline free silica content of the total dust in the study's operation environment is about 10% ~ 30%, and the respirable dust is less than 10% or undetected. The greatest difference between Foundry A and B is that Foundry A mostly has big castings, and Foundry B mostly has small castings. Small castings have a relatively shorter cooling time, and therefore Foundry B can be humidified during mold releasing to inhibit the production of dust, and the dust that can be collected in the air will largely decrease. In Foundry A's edge blushing processing area, different ratios of crystalline free silica can be collected from the respirable dust. Due to the quick rotation of the sanding wheel in the edge blushing process, the crystalline free silica in the sanding wheel, and the sand attached to the castings become smaller and spread throughout the workplace.

Crystalline free silica is more difficult to collect in the respirable dust than the total dust. The major reason for this is that the dust in foundries is mainly large particles. The study results of the study and past domestic study are very different, the reason for this may be: (1) Sample uniformity: Poor sample uniformity will easily create errors for the XRD quantitative. Therefore, to solve this problem, the study first processes a sample uniformity test on the sampler and installs a rotation plate on the analysis instrument to obtain better sample uniformity. (2) Analysis method: The analysis method used by other studies is the U.S. NIOSH 7500. This method must use a silver membrane to process filtration and background correction, and the silver membrane from different batches have

great variability, which can easily cause quantitative error. On the contrary, the analysis method used by the study is Japan's JIS A1481, which does not need to process the sample's pre-treatment. It can reduce the error caused by human factors, and at the same time, use the aluminum plate to process the intensity correction caused by processing the base standard absorption correction method for diffraction. Due to the small variability of aluminum plates, the error can also be reduced. (3) Currently, the domestic analysis methods use the 4^{th} category dust for sampling. As the crystalline free silica content percentage cannot be accurately measured, it can only take the weighing dust amount and calculate with 90-100% of the original sand purity, which has resulted in the overestimation of environmental exposure concentration. The smaller the dust particle size is, the greater the damage it will cause in lungs through breathing. It is recommended that in the future, focusing on the workplace of crystalline free silica, the allowable concentration of respirable dust standard in the air shall refer to a single value for control.

Conclusion

The study refers to Japan's 2006 analysis method, JIS A1481, to process crystalline free silica analysis, which can establish a simple, environmental friendly, low cost, and non-destructive sampling and analysis method for the exposure concentration investigations of foundries and related industries. The study found that the respirable dust content is not high in the foundry workplace. The crystalline free silica included in the respirable dust is mostly undetected or less than 10%, and the content in the total dust is mostly 10~30%, and is not the original sand purity that is commonly used by the current concentration calculation. There are quite a few workers who expose themselves to crystalline free silica due to work, therefore, hopefully, this method effectively assists in the exposure concentration investigation of the related industries to further improve the work environment and achieve the goal of protecting the environment and workers' health.

Acknowledgement

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