Journal of Air Pollution and Health (Spring 2016); 1(2):77-82

Original Article

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ENVIRONMENTAL MONITORING OF COBALT IN BREATHING ZONE OF WORKERS EMPLOYING IN A CERAMIC INDUSTRY

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ARTICLE INFORMATION

Article Chronology:

Received 23 December 2015

Revised 16 January 2016

Accepted 27 January 2016

Published 31 May 2016

Keywords:

Cobalt, Ceramic industry, Glaze, Spirometry.

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ABSTRACT:

Introduction: Glazers in ceramic industry are exposed to a variety of glazes, containing heavy metal salts, particularly cobalt. Cobalt is used in glaze to produce blue dye; therefore, occupational exposure can be taken place, causing adverse effect on the body organs. The aim of this study was to determine the concentration of cobalt in the breathing zone of 49 glazers exposed to this metal while mixing, handling, and firing processes is performed in the ceramic industry.

Materials and methods: An air sample was taken from the breathing zone of each worker continuously for 8 h on a cellulose ester membrane filter of 37 mm diameter followed by determination of cobalt concentration using Inductively Coupled Plasma-atomic Emission Spectroscopy (ICP-AES). In order to examine whether a correlation exists between work shifts, kind of job, ventilation system, and cobalt concentration, all participants filled out a self administered questionnaire. The lung function tests were also performed on each control and cobalt exposed subjects. T-tests was carried out to compare the cobalt concentrations between groups.

Results: The mean value of cobalt concentration in glazers was 5.5 times higher than the ACGIH threshold limit value (0.02 mg/m^3). Tile glazers had higher concentrations of cobalt than the pottery glazers. Spirometric parameters were significantly lower in the glazers compared to the control group ($P<0.001$).

Conclusions: This study showed high concentration of cobalt in the breathing zone of glazers that can cause decrease in spirpmetric parameters. However, further studies on co-exposure to silica and heavy metals such as cobalt in pulmonary function impairment are necessary.

INTRODUCTION

In production process of ceramic glazes, chemical compounds such as oxides, pigments, feldspars and frits are used as important materials. The frits are pre-melted glassy materials include mixtures of carbonates and silicates to lower the melting point and a metal oxide to production of colour [1-3]. These chemicals are mixed in various ra-

Kargar-Shouroki F, Shahtaheri SJ, Golbabaei F, Barkhordari A, Rahimi-Froushani A. Environmental monitoring of cobalt in breathing zone of workers employing in a ceramic industry. Journal of Air Pollution and Health. 2016; 1(2): 77-82.

tios in the powder form in the presence of water to form a suspension solution. This suspension matrix is then applied by brushing, sponging, and dripping methods to a clay body and fired at a high temperature.
To produce a blue colour, cobalt oxide can be used. Usually, the pigment and grit are ground together to form a colour powder. These colour powders are carefully mixed with glaze. Ceramic glaze seals the surface of the body to enhance hardness, environmental durability and wear resistance to a body as well as the aesthetic qualities [1-3]. Egypt and Persia are considered as the first countries tried to use cobalt as a blue colouring agent for pottery, jewelry, and glass in 2000BC. In these days, cobalt is also applied as a necessary component of blue glaze in Danish porcelain. Moreover, bright blue pigment of cobalt was used by the artist Leonardo Da Vinci in oil paints from ancient times [4]. use of blue pigments is of preference choice in the ceramic tile industries for covering the floors and walls as well as in the bulk colouration of polished, unglazed, porcelainized stoneware [5]. The main disadvantage of cobalt is its high toxicity into the body especially in workplaces that are not properly ventilated [2]. Cobalt may cause allergic contact dermatitis [6-8] cardiomyopathy [9, 10] and asthma [11-13]. The skin and the respiratory tract are target organs of the cobalt. Cobalt is not a cumulative toxin and about 80% of absorbed cobalt is excreted in urine and about 15% is excreted in feces. In order to determine the recent exposure of a worker to cobalt, it is necessary to analyze blood and urine [14]. Cobalt is classified as a possible human carcinogen by the International Agency for Research on Cancer (IARC) [15].
The present study has been organized to gain three goals: (I) to determine the mean concentration of cobalt in the breathing zone of the glazers in a ceramic industry (II): to identify relationship between the parameters including work shift, ventilation system, kind of job, and the concentration of cobalt (III): and finally to study the effect of occupational exposure in glazers on lung function.
However, exposure to some metals used in the ceramic industries have been evaluated in our previous works [16-19].

MATERIALS AND METHODS

This research was a case-control study. The subject population was consisted of 49 glazers: 33 tile glazers, 16 pottery glazers working in the glazing units of the ceramics industry. Because of the low number of glazers in each tile glazing unit, 15 tile factories were studied. All 16 pottery glazers working in several pottery workshops and a control group consisting of 55 office workers were selected for the study. In glazers, ages were ranged from 22 to 50 years with an average of 30.67 years (SD=5.88) and for control group it was from 23 to 50 years with an average of 32.6 years (SD=7.1). The control group had never been occupationally exposed to cobalt. The work shift length was 8 h, with two shifts per day. Subjects were assessed with a self administered questionnaire; comprises questions about kind of job, work shift, ventilation system, age, weight and height. There were not significant differences between glazers exposed to cobalt and the control subject concerning the age, weight, and height.
An air sample was taken from the breathing zone of each worker continuously for 8 h by a personal sampling procedure. The cobalt was collected on a cellulose ester membrane filter of 37 mm diameter. The flow rate of the pump (SKC 224) was adjusted to 2 l/min. Before the samples were taken, the pumps were calibrated by the electronic bubble meter. The blank samples were collected of workplaces. The cobalt content of both sampling filter and blank filter were determined by inductively coupled plasma absorption emission spectrophotometry (ICP-AES), (SPECTRO, ARCOS, Germany) in accordance with the NIOSH 7300 method.
Spirometry testing was carried out in 55 controls and 49 cobalt exposed subjects by using a vitalograph spirometer (model 2120). The spirometer was calibrated daily with one liter calibration syringe and operated within a temperature range

of 20-25°C. Tests were performed in a standing position and conducted according to American Thoracic Society (ATS) recommendations. In spirometric lung function tests, forced vital capacity (FVC), forced expiratory volume in one second (FEV1), forced expiratory flow (FEF_{25-75}) was measured. The FEV1/FVC ratios were calculated as percentages. Statistical analysis was performed using the SPSS 16 software. The differences between groups were evaluated by the independent samples t-tests. The level of significance was taken as $P<0.05$ for samples.

RESULTS AND DISCUSSION

Workers in ceramics industries are exposed to clay as a source of silica and aluminum oxide, feldspar, calcium carbonate, dolomite, zinc oxide, talc, kaolin zirconium silicate, magnesium carbonate, various frits and metal oxides. Prolonged periods of exposure may lead to lung function impairment [3, 20].

Table 1 shows the participants' demographic data. Mean for age, height and weight were not significantly different between groups

In the present study, all spirometric parameters in glazers significantly decreased as compared to the controls (Table 2). The highest decrease was observed in FEV1 and the ratio of FEV1/FVC. Our results showed a reduction in lung function, mainly of the obstructive syndrome type in the glazers.

Previous studies in ceramic industry have shown that occupational exposure to high concentrations of silica induces chronic obstructive pulmonary disease (COPD) and decrease spirometric parameters [21, 22]. Similar to silica, cobalt as another constituent of glazes is involved in the mechanism of chronic bronchial obstruction [23, 24]. Exposure to the cobalt blue dye among plate painters enhances respiratory symptoms and airway resistance [25]. A significant reduction in spirometric parameters were observed in workers exposed to cobalt compounds [26]. For this reason, studies integrating occupational exposure to heavy metals such as cobalt and silica may help in the assessment of risk pulmonary disfunction where co-exposure to heavy metals and silica may be occurred.

Cobalt concentration in the breathing zone was determined in 49 glazers. Mean value level was 0.11 mg/m^3 with a range between 0.01 mg/m^3 and 0.84 mg/m^3.

Table 3 gives the cobalt measurement in breathing zone of the glazers by independent factors.

None significant difference was observed between

Table 1. Population characteristics of the study groups

Parameters	**Glazers** (n = 49)		**Control** (n = 55)		
	Mean	S.D	Mean	S.D	P_{value}
Age(year)	30.67	5.88	32.6	7.1	0.12
Height(cm)	174.5	8.6	176.42	9.06	0.26
Weight(kg)	77.44	11.7	78.25	10.6	0.7
BMI	25.59	4.39	25.33	4.29	0.76

Table 2. Mean value and S.D of spirometric parameters by study groups

Parameters	Glazers (n=49)				Control (n=55)					
	Mean	S.D	Min	Max	Mean	S.D	Min	Max	t	P_{value}
FVC(L)	4.24	0.67	2.86	5.65	4.74	0.66	3.2	5.8	-4.02	<0.001
FEV1(L)	3.5	0.7	2.1	5.28	4.25	0.7	2.57	5.74	-5.58	<0.001
FEV1(percent)	80.99	8.16	58	98	88.85	5.6	80	99	-5.09	<0.001
FEF_{25-75}(L)	3.47	0.8	2.18	5.6	4.49	0.69	2.35	5.5	-7.08	<0.001

Table 3. Mean values and S.D of cobalt measured in breathing zone by independent factors.

Factor		n	Mean ± SD (mg/m^3)	t	P_{value}
Shift	Morning	25	0.01 ± 0.2	-0.29	0.77
	Evening	24	0.11 ± 0.18		
Ventilation system	Non Standard	37	0.11+0.19	0.49	0.62
	Standard	12	0.08 ± 0.17		
Kind of Job	Pottery Glazer	16	0.06 ± 0.07	-1.77	0.08
	Tile Glazer	33	0.13 ± 0.21		

the amount of cobalt in the morning and evening shifts (P=0.77) (Table 3). Glazers who worked in well ventilated places showed lower levels of cobalt as compared to the glazers who worked in poorly ventilated areas (0.08 mg/m^3 versus 0.11mg/m^3), however, this difference was not statistically significant (P=0.62) (Table 3).
The pottery glazers had an average of 0.06 mg/m^3 and for the tile glazers, the average was 0.13 mg/m^3. The tile glazers had higher concentrations of cobalt than the pottery glazers (P=0.08) (Table 3).
In this study, the levels of exposure to cobalt were much higher than the ACGIH threshold limit value (0.02 mg/m^3) [27]. These results was also observed at several ceramic factories [28]. Another study among plate painters exposed to cobalt blue dyes revealed increase urinary cobalt content in comparison to the control group [29]. Results of another study showed that, women who are exposed to cobalt blue dye may be at slightly increased risk of developing lung cancer than the expected value [30].
Glazers who worked in well ventilated places, because of less inhalation of cobalt dust, had a lower cobalt level as compared to the work in poorly ventilated places. Similar study has reported, high hair cadmium and lead concentrations in glazers in unventilated places [31]. In our study, non-significance of this decline might be due to the low number of ventilated places. Since condition of workplaces such as ventilation system and glaze constituents did not change in the shifts, significant difference between groups in relation to shift had not been observed. The higher cobalt level in the tile glazers showed more exposure to cobalt. This was taken place because glaze constituents had a high percentage of this metal. Indeed, at the time of this study, cobalt pigments largely was used to produce blue color in tiles [3].
If glazes are improperly formulated and fired, the component of glazes not adhere to the clay body and release in contact with food and poisoning can occur in the general population during household use [1, 3]. Several studies reported that, acidic food and juice induce leaching of cobalt from glaze [32, 33, 34].

CONCLUSIONS

This study showed high concentration of cobalt in the breathing zone of glazers that can cause decrease in spirpmetric parameters. However, further studies on co-exposure to silica and heavy metals such as cobalt in pulmonary function impairment are necessary. Workers should use respirators and separate work clothes than other clothes to prevent contamination.

FINANCIAL SUPPORTS

This research has been supported by Tehran University of Medical Sciences and Health Services grant (project no. 11/2/88/8911).

COMPETING INTERESTS

The authors declare that there is no conflict of interest.

ACKNOWLEDGEMENTS

The authors would like to thank Tehran University of Medical Sciences for financial support of this study.

ETHICAL CONSIDERATIONS

Ethical issues (Including plagiarism, Informed Consent, misconduct, data fabrication and/or falsification, double publication and/or submission, redundancy, etc) have been completely observed by the authors.

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