Assessment of Chemical Hazard from Decoration Firing Kiln in a Benjarong Porcelain Manufacturing Community Enterprise

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ABSTRACT

Benjarong porcelain is a unique Thai pottery. It represents the art and culture of Thailand for hundreds of years. The decorating pattern uses various colors, including metal oxide, glue and gold paint. In the firing process, chemical emissions are produced from the kiln, which have not been studied before. From the literature review, the potential pollutants comprise hydrogen cyanide, formaldehyde, metal fumes and flue gases. This study assessed the type and concentration of chemicals emitted from Benjarong decoration firing kiln. One voluntary Benjarong enterprise, using regular decoration firing, was selected as the study site. Air samples were collected and analyzed for hydrogen cyanide, formaldehyde, heavy metals, i.e., lead (Pb), nickel (Ni) and cadmium (Cd) and flue gases inside, beside and behind the kiln storage room, respectively. The result showed that all chemical concentrations were lower than the Occupational Exposure Limit (OEL) of the U.S.OSHA standard. However, the maximum concentration of Pb was quite close to the OEL standard value at 0.044 mg/m^3 showing that the greatest health risk in Benjarong production is Pb exposure.

Keywords: Benjarong porcelain, kiln emission, decoration firing, chemical hazard

J Public Health 2017; 47(3): 264-275

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Introduction

Benjarong porcelain has been one of the famous arts and handicrafts of Thailand for hundreds of years. It comprises painted porcelain representing the uniqueness of local and ancient history. Most products are bowls, cups and various souvenirs. The production is centered in Suphanburi, Nakhon Pathom, Samut Sakhon and Samut Songkham Provinces and operates as a community business.[1, 2] The process begins with clay forming then firing at the proper temperature (1,150-1,280^{o}C), called bisque firing. Then the products are painted with five different colors. Moreover, the products are decorated with gold paint, which is a mixture of pure gold to make them even more beautiful. Finally, they are fired again at 700 – 800^{o}C four to six hours, which is called decoration firing and are subsequently ready to sell.

The preliminary survey of Benjarong production revealed that the emissions from decoration firing produced a foul smell. Workers were disturbed and express signs and symptoms such as sore throat, dizziness etc.[3] Gold paint is expected to contain hydrogen cyanide because it is used as a solvent to extract gold from ore.[4, 5] Numerous articles have shown the dangers of ceramic kiln emissions in the air included particulate matters, soot and gases, e.g., carbonoxides, nitrogen oxides, sulfur oxides, inorganic fluorine and chlorine compounds, volatile organic compounds (VOCs), formaldehyde and its derivatives and heavy metals, e.g., Cd, Ni and Pb.[6]

Benjarong porcelain containing gold paint is expected to emit hydrogen cyanide because this chemical is commonly used to extract gold from ore.[4, 5] formaldehyde and its derivatives are used as preservatives in paint and glue. Also, the organic materials in clay may decompose to form formaldehyde when glazed.[7] Heavy metal fumes are produced from color pigment. Flue gas including carbon monoxide (CO), nitrogen oxide (NO), nitrogen dioxide (NO_2) and sulfur dioxide (SO_2) have been reported as emissions from the decoration firing process.[5, 6]

The literature review showed health hazards from Benjarong production such as eye irritation, skin irritation and shoulder, arm, knee and leg pain. Especially, neck pain was the most common.[8] The hazards of chemicals especially VOCs include headache and dizziness.[3] Even some studies have shown the chemicals emitted from the Benjarong kiln also represent serious health issues that have received less attention.[8] Therefore, the objective of this study was to assess the type and concentration of chemicals emitted from the Benjarong decoration firing kiln.

Methods

One voluntary Benjarong enterprise in Amphawa District, Samut Songkram Province, Thailand was selected as the study site. The electric kiln for decoration firing was located in a room with a ventilation fan installed at the back wall. During the process, the kiln door is slightly opened to release emitted chemicals until 400°C then it closes. The air sampling points were selected at the inside, beside and behind the kiln room. The air flows in these sampling points were small and expected not to disturb the air sampling. The sampling started from the firing process until the kiln was closed which takes about five hours. The sampling was repeated five times for five batches of firing. The type and weight of Benjarong at each firing time is shown in Table 1. Hydrogen cyanide, Formaldehyde, Heavy Metal fumes (Pb, Ni, Cd) and Flue gases (CO, NO, NO_2, SO_2) were analyzed in each sampling.

Table 1 The Characteristics of Benjarong Porcelain at Each Air Sampling.

No of samplings	Type of Benjarong Porcelain	Total Weight (g)	Time of Decoration Firing (min)
1	Vase, Vase Thick Coating, Cartridge, Kettles, Lid, Tea Cup, Tray	12,078	150
2	Coffee Cup, Kettles, Jar, Lid, Tray, Cup	13,452	240
3	Lid of Cinerary Urn, Cinerary Urn, Glass, Glass Lid, Saucer, Picture, Ancient Jar Lid	16,416	180
4	Elephant Mug, Dish, Glass Lid, Saucer	8400	180
5	Glass, Jar, Jar Lid, Tea Cup, Plate, Glass Lid, Saucer, Small Elephant, Elephant Round, Cinerary Urn, Cinerary Urn Lid	13,374	180

To collect the hydrogen cyanide gas, the NIOSH Method 7904 was followed. The sampling pump was connected to an impinger containing 0.1N potassium hydroxide (KOH) solution. This solution was analyzed using the NIOSH Method 6010. The samples reacted with barbituric acid – pyridine reagent and the products were measured by spectrophotometer at 580 nm (Thermo Scientific, Helios OMEGA).

Three heavy metal fumes, i.e., Cd, Ni and Pb were selected to measure because they mostly contained used pigment.[6] The air sampling pump was connected to a 0.8 µm, cellulose ester membrane matched filter. The membranes were digested and analyzed by Inductively Coupled Argon Plasma, Atomic Emission Spectroscopy (ICP-AES) (Optima™ 8000, PerkinElmer) and Flame Atomic Absorption Spectrophotometer (Thermo Scientific, Helios OMEGA).

Formaldehyde was collected using sorbent tubes (SKC) containing 2-(hydroxymethyl) piperidine-coated XAD-2 and the oxazolidine derivative of formaldehyde was analyzed using Gas Chromatography with Flame Ionization Detector (GC-FID) (Agilent Technologies, 7890B) according to the NIOSH Method 2541. All tubes were stored at 4°C before and after sampling. Toluene was used as a desorption solvent. The column was the DB-Wax bonded phase (30 m x 0.32-mm ID, 0.5-µm film).

Flue gas including CO, NO, NO_2 and SO_2 were measured by Testo 350 Portable Emission Analyzer (TESTO, INC.) The analyzer had been calibrated by gas standard including O_2, CO, NO) and nitrogen NO_2. These flue gases were measured every 15 minutes from the start of firing until the kiln door was closed. The calibration curves of all chemical standard solutions were freshly prepared except for formaldehyde where the repeated analyses of the standard solutions showed stable results for the whole period of experiment. All calibration curves were found to be linear with R^2 more than 0.99.

The data were analyzed using SPSS for Windows, version 18. Descriptive analysis was used to describe maximum, minimum and average chemical concentrations. Bivariate analysis was used to correlate weight and chemical concentrations ($p < 0.05$). This research passed the ethics review, COA No. MUPH 2016-076 from the Board of Ethics in Human Research, Faculty of Public Health, Mahidol University.

Results

Hydrogen cyanide

The concentrations of hydrogen cyanide emitted from the kiln storage room are shown in Table 2. The maximum concentrations found at inside, beside and behind the kiln were 0.0018, 0.0003 and 0.0007 mg/m^3, respectively. The minimum concentration inside the storage room was 0.0001 mg/m^3 whereas beside and behind concentrations were nondetectable (ND). However, compared with the OSHA standard, the concentration of hydrogen cyanide was still very low. The correlation between weight of Benjarong porcelain and concentrations of hydrogen cyanide inside, beside and behind the kiln storage room was not significant at p 0.510, 0.709, 0.430, respectively.

Table 2 Concentrations of Hydrogen Cyanide at Each Sampling Time.

No.	Concentration of HCN-(mg/m^3)		
	Inside the kiln room	Beside the kiln room	Behind the kiln room
1.	0.0013	ND	0.0004
2.	0.0001	ND	ND
3.	0.0018	0.0003	0.0007
4.	0.0007	0.0002	0.0002
5.	0.0005	0.0002	0.0001
Average	0.0009	0.00014	0.0003

Note: OHSA standard of HCN^- for 11 mg/m^3, ND = Not Detected

Formaldehyde

The concentrations of formaldehyde emitted from the kiln storage room are shown in Table 3. The maximum concentrations found inside, beside and behind the kiln storage room were 0.064, 0.0113 and 0.0172 mg/m^3, respectively. The minimum concentrations of the three areas were ND. However, concentrations of formaldehyde did not exceed the OSHA standard. The correlation between weight of Benjarong porcelain and concentration of formaldehyde inside, beside and behind the kiln storage room was not significant at p 0.973, 0.281 and 0.360, respectively.

Table 3 Concentrations of Formaldehyde at Each Sampling Time.

No.	Concentration of formaldehyde (mg/m^3)		
	Inside the kiln room	Beside the kiln room	Behind the kiln room
1	0.064	ND	ND
2	0.0294	0.0104	ND
3	ND	ND	ND
4	0.0494	0.0113	0.0150
5	0.031	ND	0.0172
Average	0.0348	0.0043	0.0064

Note: OHSA standard of formaldehyde for 0.75 mg/m^3, ND = Not Detected

Metal fumes

The concentrations of Pb, Ni and Cd fumes emitted from kiln storage room are shown in Table 4.

The maximum concentrations of Pb fumes found inside, beside and behind the kiln storage room were 0.0443, 0.0071, and 0.0066 mg/m^3, respectively and the minimum concentration was ND. The correlation between weight of Benjarong porcelain and concentration of Pb fumes inside, beside, and behind the kiln storage room was not significant at p = 0.716, 0.905, and 0.976, respectively.

The maximum concentrations of nickel fumes inside, beside and behind the kiln storage room were 0.0025, 0.0037, and 0.0046 mg/m^3, respectively and the minimum of the three areas was ND. The correlation between weight and concentration of Ni fumes inside, beside and behind the kiln storage room was not significant at p 0.848, 0.880, and 0.919, respectively.

The maximum concentrations of cadmium fumes inside, beside, and behind the kiln storage room were 0.0012, 0.0009, and 0.0014 mg/m^3, respectively. The minimum concentration inside the kiln storage room was 0.0006 mg/m^3 and the two remaining areas were ND. The correlation between weight of Benjarong porcelain and concentration of Cd fumes inside, beside and behind the kiln storage room was not significant at p 0.716, 0.905, and 0.976, respectively.

Flue Gas

The flue gas emissions including CO, NO, NO_2, and SO_2 are shown in Figure 1.

The results showed that the maximum concentration was 3 ppm beside the kiln storage room, which was very low compared with the 50 ppm standard. The maximum concentration of NO was 1 ppm and did not exceed the 25 ppm standard . The maximum concentration of NO_2 was 0.2 ppm found inside the kiln room while the other concentrations were ND. $SO_2$was not detected in the three areas at all five sampling times.

Table 4 Concentrations for Each Metal Fume Site.

NO.	Heavy Metal Fume	Area Sampling		
		Inside the kiln storage room (mg/m^3)	Beside the kiln storage room (mg/m^3)	Behind the kiln storage room (mg/m^3)
1.	Pb	0.0443	0.0071	0.0066
2.	Pb	0.0300	0.0015	0.0048
3.	Pb	0.0023	ND	ND
4.	Pb	0.0121	ND	ND
5.	Pb	0.0146	0.0018	0.0005
Average	Pb	0.0207	0.0021	0.0024
1.	Ni	0.0025	0.0037	0.0046
2.	Ni	0.0002	0.0010	0.0022
3.	Ni	ND	ND	ND
4.	Ni	ND	ND	ND
5.	Ni	ND	ND	ND
Average	Ni	0.0005	0.0009	0.0014
1.	Cd	0.0012	0.0009	0.0014
2.	Cd	0.0010	0.0002	0.0004
3.	Cd	0.0006	ND	ND
4.	Cd	0.0006	0.0002	0.0001
5.	Cd	0.0008	0.0003	0.0002
Average	Cd	0.0008	0.0003	0.0004

Note: OSHA Standard of Cd, Ni, Pb for 0.005, 1, 0.05 mg/m^3 respectively, ND: Not Detected

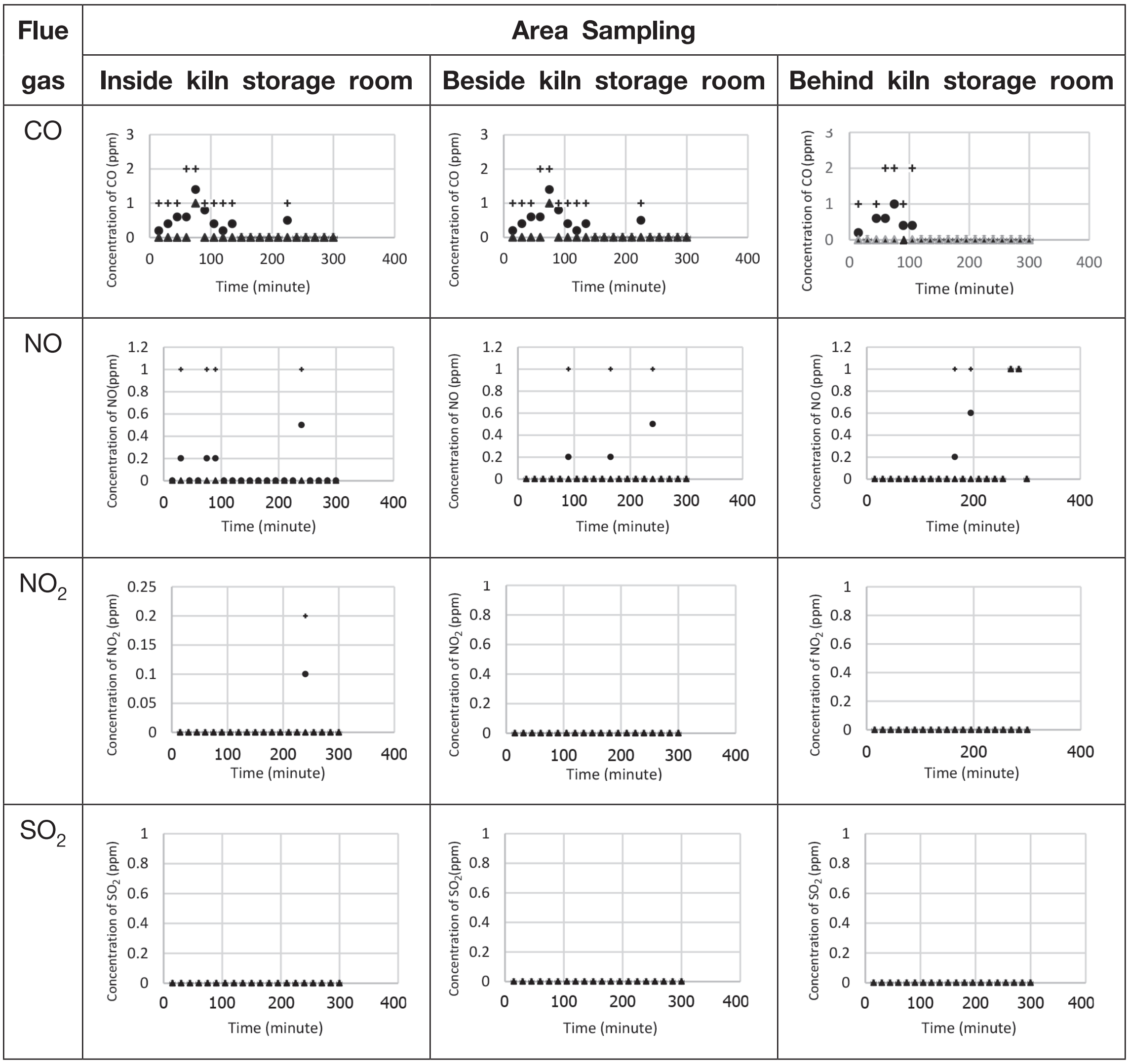

Figure 1 Concentration of Flue Gas Inside, Beside, and Behind Kiln Room.

Note: The plus sign represents the maximum value of the circle representing the average and the triangle represents the minimum.

Discussion

The emitted hydrogen cyanide concentrations were not at a hazardous level. The very low concentrations were due to the very small amounts of gold paint used in Benjarong porcelain production. In addition, some amount of hydrogen cyanide may evaporate during the painting process. Occupational exposure to cyanide is found in industries such as electroplating in jewelry polishing, gold and silver extraction, metallurgy, tanning, photography, and fumigation of pesticides/rodenticides[9].

Exposures to cyanide are possessed by the central nervous system and create cardio-vascular disturbances. General signs and symptoms include tachypnea, headaches, vertigo, lack of motor coordination, weak pulse, cardiac arrhythmias, vomiting, stupor, convulsions etc[10]. The EPA has established a reference concentration (RfC) of 3 μgm^{-3} (2.67 ppb) to protect against the toxic effects of long-term inhalation exposures to hydrogen cyanide in air (USEPA, 1994b)[11].

This study showed formaldehyde was emitted by the kiln. Many sources of formaldehyde are found in ceramic ware. Formalin and other formaldehyde derivatives are used as preservatives as well as paints and glues causing formaldehyde to be released during firing. Furthermore, formaldehyde can be released when organic materials are burned in a kiln.[12]

All measured heavy metal fumes did not exceed the standard. However, the concentration of Pb in the kiln room was quite close to the standard indicating Pb is the most released metal fume from Benjarong ware. This was related to much research showing Pb was the major heavy metal fume produced in the decoration firing process.[6, 13] Pb is a cumulative toxicant that affects multiple body systems and is particularly harmful to young children. After being distributed to the brain, liver and kidneys it becomes stored in the teeth and bones, and accumulates over time. Human exposure is usually assessed using the amount of Pb found in the blood.

This study found low concentrations of CO emitted from the kiln. These low levels were suspected to have derived by having sufficient oxygen for firing supplied by a ventilated fan at the back wall. In addition, low concentrations of NO and NO_2 were found. This may be because NO and NO_2 are released from combustion at high temperatures (especially >1200°C). This study did not discover SO_2 in flue gas from firing. Typically, SO_2 is associated with fuel and sulfur in raw materials.[6] However in this study, an electric kiln was used and sulfur existing in raw material was not affected due to the two firings before.

Conclusion

This research measured the concentration of pollutants in air during decorative firing. These included hydrogen cyanide, formaldehyde, Pb, Ni, Cd and flue gases. This showed that all pollutant concentrations were below the standard. Pb was near the OHSA standard. Therefore, workers should wear masks when working near the kiln. However, the outside area of the kiln storage room showed low concentrations of chemical emission probably due to adequate ventilation.

Even though this study investigated the health effects of chemical exposure from decoration firing were not significant, some chemicals such as formaldehyde and VOCs were not measured in this study. Because a significant amount of these chemicals have been discussed in related literature, these should be explored in future studies.

Acknowledge

This research was funded by the Thailand Research Fund and was graciously allowed to use Coupled Argon Plasma, Atomic Emission Spectroscopy (ICP-AES) from the Armed Forces Research Institute of Medical Sciences.

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การประเมินการสัมผัสอันตรายจากสารเคมีในกลุ่มวิสาหกิจชุมชนหัตถกรรมเครื่องเบญจรงค์

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บทคัดย่อ

เครื่องเบญจรงค์เป็นเครื่องปั้นดินเผาที่มีความเป็นเอกลักษณ์ แสดงถึงศิลปะและวัฒนธรรมของประเทศไทยที่สั่งสมมายาวนาน การตกแต่งลวดลายจะใช้สีต่างๆที่มีส่วนประกอบของออกไซด์ของโลหะ กาว และน้ำทอง จากนั้นจะนำไปเผาปัจจุบันยังไม่มีงานวิจัยเกี่ยวกับชนิดและความเข้มข้นของสารมลพิษจากการเผานี้ การทบทวนวรรณกรรมของงานเซรามิกที่คล้ายคลึงกันพบว่า สารมลพิษคือ สารไฮโดรเจนไซยาไนด์ ฟอมัลดีไฮด์ ฟูมโลหะ และแก๊สเผาไหม้ จึงนำสู่วัตถุประสงค์ของงานวิจัยคือ ศึกษาชนิดและความเข้มข้นของสารมลพิษจากเตาเผาเครื่องเบญจรงค์ในกลุ่มวิสาหกิจชุมชนเครื่องเบญจรงค์ 1 กลุ่ม โดยเลือกจากความสมัครใจและมีการเผาเครื่องเบญจรงค์เป็นประจำ และเก็บตัวอย่างอากาศเพื่อวิเคราะห์หาสารไฮโดรเจนไซยาไนด์ ฟอมัลดีไฮด์ ฟูมโลหะ (ตะกั่ว, นิกเกิล, แคดเมียม) และแก๊สเผาไหม้ ในบริเวณ 3 จุด คือ บริเวณในห้อง ข้างห้อง และหลังห้องเก็บเตาเผา ผลของงานวิจัย พบว่า ความเข้มข้นทั้งหมดเปรียบเทียบกับค่ามาตรฐานของ OHSA ไม่มีสารใดเกินค่ามาตรฐาน อย่างไรก็ตามความเข้มข้นสูงสุดของตะกั่วมีค่าใกล้เคียงกับค่ามาตรฐานมากคือ 0.044 มก/ลบ^3 ดังนั้นพนักงานในกลุ่มเครื่องเบญจรงค์จึงมีความเสี่ยงด้านสุขภาพในการสัมผัสสารตะกั่ว

คำสำคัญ: เครื่องเบญจรงค์, มลพิษจากเตาเผา, การเผาหลังตกแต่ง, อันตรายจากสารเคมี

วารสารสาธารณสุขศาสตร์ 2560; 47(3): 264-275

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