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**LEAD PARTICULATE GENERATED FROM RUBY HEAT TREATMENT
IN CHANTHABURI PROVINCE**



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**A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Environmental Management**

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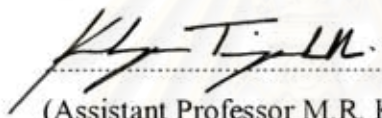
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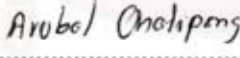
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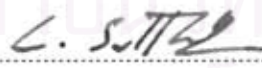
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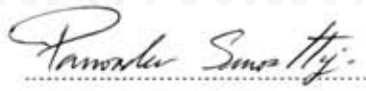
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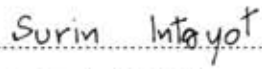
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ประเทศไทย จนถึงปัจจุบันมีการวิพากษ์วิจารณ์เกี่ยวกับการใช้แก้วตะกั่วในอุตสาหกรรมนี้ท่ามกลาง
นักวิชาการสิ่งแวดล้อมและนักอัญมณีวิทยาจำนวนมาก ดังนั้นงานวิจัยนี้จึงเป็นงานแรกที่ทำการศึกษา
การปนเปื้อนของตะกั่วในอนุภาคฝุ่นละอองจากกระบวนการเผาพลอยทับทิมโดยใช้แก้วตะกั่ว
สถานที่ที่ใช้ทำการศึกษา คือ โรงงานเผาพลอยทับทิม 2 โรงงานในจังหวัดจันทบุรี โดยแผนการศึกษา
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เผาพลอยในขณะปฏิบัติงาน และ 3) ปริมาณของตะกั่วในอนุภาคฝุ่นละอองภายในบริเวณโรงงาน ผล
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จากการศึกษาผลกระทบของตะกั่วที่คนเผาพลอยได้รับ พบว่าขั้นตอนการผสมพลอยกับแก้วตะกั่ว
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คนเผาพลอยก็มีโอกาสที่จะได้รับสารตะกั่วเพิ่มมากขึ้นเช่นเดียวกัน และจากผลการตรวจวัดความ
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ปัจจัยสำคัญต่อการเพิ่มขึ้นของปริมาณตะกั่วภายในโรงงาน แต่ระบบระบายการอากาศที่มี
ประสิทธิภาพและการแบ่งพื้นที่ในการปฏิบัติงานออกจากพื้นที่อยู่อาศัยนั้นสามารถลดผลกระทบที่จะ
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ลายมือชื่อนิสิต..... สุริย์พร ชื่นจิตต์
ลายมือชื่ออาจารย์ที่ปรึกษาวิทยานิพนธ์หลัก..... อรุณภ โชติพงษ์
ลายมือชื่ออาจารย์ที่ปรึกษาวิทยานิพนธ์ร่วม.....

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KEY WORDS: LEAD GLASS/ HEAT TREATMENT/ RESPIRABLE PARTICULATE

SUREEPORN CHUENJIT: LEAD PARTICULATE GENERATED FROM
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THESIS PRINCIPAL ADVISOR: ARUBOL CHOTIPONG, Ph.D., THESIS

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Lead glass heating has been long used in the gem industry in Thailand. Recently, it has become a concern to environmental scientists and the gemologist communities because of its dangers to health and the environment. Hence, determination was made of lead concentration in respirable particulate from the process of ruby heat treatment involving lead glass. Two home factories in Chanthaburi Province were selected for the sampling sites. Three parts of sample collections including 1) emission profile of lead from the ruby treatment furnace, 2) exposure of the treater to lead in the home factory and 3) lead concentration in indoor air of the home factory. The results show that lead particulate can emit from the furnace only during gate opening period and the highest concentrations were found within the first 10 min after gate opening. In addition, lead particulate emitted from furnace increases as amount of lead additive or ruby increases. Regarding determination of lead exposure to the treater and residents, the results clearly indicate that both mixing step and opening period of furnace are the main periods of lead exposure. Moreover, higher amounts of lead additive added into the process appear to emit higher amounts of lead. For indoor lead concentration, ruby heat treatment using lead glass clearly elevates the lead concentration within the home factory and providing an efficient ventilation system and separating the treatment area from living area can reduce the effect of lead from the process.

Field of Study:..Environmental Management..

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CONTENTS

| | page |
|---|------|
| Abstract (Thai)..... | iv |
| Abstract (English)..... | v |
| Acknowledgements..... | vi |
| Contents..... | vii |
| List of Tables..... | xi |
| List of Figures..... | xiii |
| List of Abbreviations..... | xvi |
| | |
| CHAPTER I INTRODUCTION | |
| 1.1 General Statement..... | 1 |
| 1.2 Objectives..... | 3 |
| 1.3 Hypotheses..... | 4 |
| 1.4 Scope of the Study..... | 4 |
| | |
| CHAPTER II THEORETICAL BACKGROUND AND LITERATURE REVIEWS | |
| 2.1 Ruby..... | 5 |
| 2.1.1 Chemical Composition and Structure..... | 5 |
| 2.1.2 Properties..... | 6 |
| 2.1.2.1 Physical Properties..... | 6 |
| 2.1.2.2 Chemical Properties..... | 7 |
| 2.1.2.3 Optical Properties..... | 8 |
| 2.2. Ruby Enhancement..... | 9 |
| 2.2.1 Flux-Healing Method..... | 10 |
| 2.2.2 Lead-Glass Healing Method in Chanthaburi, Thailand..... | 13 |
| 2.3 Air Pollution from Ruby Enhancement Process..... | 17 |
| 2.4 Particulates Matter (PM)..... | 18 |
| 2.4.1 Definition..... | 18 |
| 2.4.2 Size of Particulates Matter..... | 18 |
| 2.4.3 Routes of Human Exposure..... | 20 |

page

| | |
|---|----|
| 2.4.4 Human Health Adverse Effects | 20 |
| 2.5 Lead | 22 |
| 2.5.1 Chemical and Physical Properties | 22 |
| 2.5.2 Lead from High Temperature Processes | 22 |
| 2.5.3 Routes of Human Exposure | 23 |
| 2.5.3.1 Inhalation | 23 |
| 2.5.3.2 Ingestion | 23 |
| 2.5.4 Human Health Adverse Effects | 24 |
| 2.5.4.1 Acute Effect | 24 |
| 2.5.4.2 Chronic Effect | 24 |
| 2.5.5 Occupational Health Standard for Lead | 27 |
| 2.5.6 Ambient Air Quality Standard for Lead | 27 |
| 2.6 Literature Reviews | 28 |

CHAPTER III METHODOLOGY

| | |
|---|----|
| 3.1 Sampling Plan | 31 |
| 3.1.1 Emission Profile | 31 |
| 3.1.2 Exposure of the Treater to Lead Particulate | 33 |
| 3.1.3 Indoor Lead Particulate | 33 |
| 3.2 Apparatus | 34 |
| 3.2.1 Personal Air Sampling Pump | 34 |
| 3.2.2 Filter Cassette | 34 |
| 3.2.3 Filter Paper | 35 |
| 3.3 Sampling Sites | 36 |
| 3.3.1 Factory A | 36 |
| 3.3.1.1 General Background | 36 |
| 3.3.1.2 Sampling Sites | 37 |
| 3.3.2 Factory B | 38 |
| 3.3.2.1 General Background | 38 |

| | |
|-----------------------------|----|
| 3.3.2.2 Sampling Sites..... | 40 |
| 3.3.3 Internet Café..... | 41 |
| 3.3.4 Restaurant..... | 41 |
| 3.4 Digestion Method..... | 42 |

CHAPTER IV RESULTS AND DISCUSSION

| | |
|---|----|
| 4.1 Emission Profile of Lead Particulate from the Furnace..... | 43 |
| 4.1.1 Each Step of Lead-Glass Heat Treatment Process..... | 43 |
| 4.1.2 The Gate Opening Period..... | 48 |
| 4.1.2.1 Factory A..... | 49 |
| 4.1.2.2 Factory B..... | 52 |
| 4.1.3 Estimations of Lead Additive and Emission..... | 56 |
| 4.1.3.1 Estimation of Lead Additive..... | 56 |
| 4.1.3.2 Estimation of Lead emission..... | 61 |
| 4.2 Exposure of the Treater to Lead Particulate..... | 65 |
| 4.2.1 Personal Lead exposure during monitoring period..... | 68 |
| 4.2.2 Personal Lead Exposure during Ruby Treatment Process..... | 69 |
| 4.3 Indoor Lead Particulate in Home Factories..... | 70 |
| 4.3.1 Background Lead Concentration..... | 71 |
| 4.3.2 Indoor Lead Concentration in Factory A and B..... | 72 |

CHAPTER V CONCLUSIONS AND RECCOMMENDATION

| | |
|---|----|
| 5.1 Emission Profile..... | 77 |
| 5.2 Estimations of Lead Additives and Emission..... | 77 |
| 5.2.1 Estimation of Lead Additive..... | 77 |
| 5.2.2 Estimation of Lead Emission..... | 77 |
| 5.3 Exposure of Treater to Lead Particulate..... | 78 |
| 5.4 Indoor Lead Particulate in Ruby-Treatment Home Factories..... | 79 |
| 5.5 Monitoring and Standard..... | 79 |

| | page |
|-----------------|------|
| REFERENCE..... | 81 |
| APPENDICES | |
| APPENDIX A..... | 87 |
| APPENDIX B..... | 96 |
| BIOGRAPHY..... | 99 |



สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

LIST OF TABLES

| Table | page |
|--|-------------|
| 2.1 Blood Lead Levels and associated health and physiological effects in children and adults | 26 |
| 2.2 OSHA, NIOSH and ACGIH occupational health standards for lead | 27 |
| 2.3 Thailand occupational health standards for lead | 27 |
| 2.4 Ambient Air Quality Standard for Lead | 27 |
| 4.1 Lead particulate concentration (mg/m^3) from heat treatment process at different sampling periods | 45 |
| 4.2 Estimation of lead concentration emitted during an hour after opening period using results from B* and B sampling rounds | 47 |
| 4.3 Estimation of lead concentration emitted during an hour after opening period using results from C and C* sampling rounds | 47 |
| 4.4 Average estimated lead concentration (mg/m^3) during an hour after gate opening | 48 |
| 4.5 Lead concentration (mg/m^3) in particulate matter emitted in each ten minutes during an hour after gate opening from Furnace A-1 | 49 |
| 4.6 Lead concentration (mg/m^3) in particulate matter emitted in each ten minutes during an hour after gate opening from Furnace A-2 | 51 |
| 4.7 Lead concentration (mg/m^3) in particulate matter emitted in each ten minutes during an hour after gate opening from Furnace B-1 | 53 |
| 4.8 Lead concentration (mg/m^3) in particulate matter emitted in each ten minutes during an hour after gate opening from Furnace B-2 | 54 |
| 4.9 Weight of lead additive and emission concentration monitored at the first 10 min after gate opening from Furnaces A-1 and A-2 | 56 |
| 4.10 Prediction of lead additive used in ruby treatment process compared with real record from Factory A | 60 |
| 4.11 Weight of ruby (kg) and lead concentration (mg/m^3) emitted within the first 10 min after gate opening, data from Factories A and B | 61 |
| 4.12 Estimation of lead concentration emission within first 10 min after gate opening using equations 4.5 to 4.8 | 64 |

| Table | page |
|---|-------------|
| 4.13 Personal exposure of the treater to lead concentrations (mg/m^3) during whole day monitoring, mixing step, and gate opening step at Factory A..... | 67 |
| 4.14 Personal exposure to lead (mg/m^3) for the treater during resident period, mixing step and gate opening step at Factory B..... | 68 |
| 4.15 Indoor lead particulate concentrations (mg/m^3) of background collected from internet café and restaurant..... | 72 |
| 4.16 Indoor lead particulate concentrations (mg/m^3) in Factory A at three different sampling periods and whole day average..... | 74 |
| 4.17 Indoor lead particulate concentrations (mg/m^3) in Factory B at three different sampling periods and whole day average..... | 76 |

LISTS OF FIGURES

| Figure | page |
|--|-------------|
| 2.1 Three different views of the structure of corundum, the top illustration shows the looking down the <i>c</i> axis, while below is a view perpendicular to the <i>c</i> axis. At right is a perspective view..... | 6 |
| 2.2 (a) The centuries old technique of blow-pipe heat treatment of ruby in Sri Lanka (b) Primitive charcoal oven at Chathaburi town, Thailand..... | 10 |
| 2.3 Diagram showing some typical clarity imperfections in ruby..... | 11 |
| 2.4 Diagram of a flux-healed fracture..... | 12 |
| 2.5 Schematic diagram of lead-filled treatment..... | 13 |
| 2.6 (a) Ruby soaked with lead-glass additives (b) Loading ruby mixed with lead-glass additives into crucibles..... | 15 |
| 2.7 Electric furnace used in Chathaburi province, Thailand..... | 15 |
| 2.8 Heat treatment condition of ruby involving lead-glass compound..... | 16 |
| 2.9 (a) Rough, (b) pre-forms, and (c) after first heating of ruby..... | 16 |
| 2.10 (a) Removal of the ruby from the crucible (b) Glued ruby after lead-glass filled heat treatment..... | 17 |
| 2.11 Air pollution generated from ruby enhancement process..... | 17 |
| 2.12 (a) The major anatomical features of the human respiratory tract (b) The terminal bronchial alveolar structure of the human lung..... | 21 |
| 3.1 Schematic diagram of sampling plan under this thesis..... | 32 |
| 3.2 GilAir-5 constant flow air sampling pump used during this research project..... | 34 |
| 3.3 Filter cassette assembly used in this study..... | 35 |
| 3.4 (a) Top view plan of the third floor in Factory A and (b) partitioning within the ruby heat treatment room..... | 36 |
| 3.5 Electric furnaces in the ruby heat-treatment room of Factory A..... | 37 |
| 3.6 (a) Vent holes and (b) 2-slatted window and a ventilator in Factory A..... | 37 |
| 3.7 Sampling site at Factory A located above the gate of electric furnace..... | 37 |

| Figure | page |
|--|-------------|
| 3.8 Indoor sampling sites in Factory A: (a) beside a table in dining room on the first floor and (b) in front of the treater's bedroom on the third floor..... | 38 |
| 3.9 (a) Top view plan of the first floor and (b) mezzanine engaged for ruby heat-treatment in Factory B..... | 39 |
| 3.10 (a) Small vent holes above the front door and (b) back door downstairs on the first floor..... | 39 |
| 3.11 (a) Three windows always closed and (b) wall vent holes on the mezzanine..... | 39 |
| 3.12 Electric furnaces used (a) on the first floor and (b) on mezzanine..... | 40 |
| 3.13 Sampling sites for indoor dust (a) on the first floor and (b) on the third floor..... | 40 |
| 3.14 (a) Internet café taken as background location and (b) its top view plan of the first floor showing sampling site in the dining area..... | 41 |
| 3.15 (a) Restaurant used as another background location and (b) its top view plan of the first floor showing sampling site in the restaurant..... | 42 |
| 4.1 Sampling rounds in each step (heating up, soaking, and cooling down) of ruby heat treatment process..... | 44 |
| 4.2 Lead particulate concentrations (mg/m^3) from heat treatment process..... | 45 |
| 4.3 Six sampling rounds for 10 min each during an hour after gate opening..... | 48 |
| 4.4 Lead concentrations (mg/m^3) emitted during an hour after gate opening period from Furnace A-1..... | 50 |
| 4.5 Lead concentrations (mg/m^3) emitted during an hour after gate opening period from Furnace A-2..... | 51 |
| 4.6 Lead concentrations (mg/m^3) emitted during an hour after gate opening period from Furnace B-1..... | 53 |
| 4.7 Lead concentrations (mg/m^3) emitted during an hour after gate opening period from Furnace B-2..... | 55 |

| Figure | page |
|--|-------------|
| 4.8 The relation between weight of lead additive and lead concentration emitted from the furnace including the fitting of linear equations of (a) Furnace A-1 and (b) Furnace A-2..... | 58 |
| 4.9 The relation between weight of lead additive and lead concentration emitted from the furnace including the fitting of linear equations of raw data (a) and averaged values (b) obtained from Furnaces A-1 and A-2..... | 58 |
| 4.10 The relation between ruby weight and lead concentration emitted from the furnace including the fitting of linear equations of available data from Factory A (a) and Factory B (b)..... | 62 |
| 4.11 The relation between weight of ruby and lead concentration emitted from the furnace including the fitting of linear equations of raw data from both Factories A and B (a) and their average data (b)..... | 63 |

LIST OF ABBREVIATIONS

| | |
|-------------------|---|
| AAS | Atomic Absorption Spectrometer |
| ACGIH | The American Conference of Governmental Industrial |
| AGL | American Gemological Laboratories |
| ALA-D | Aminolevunic Acid Dehydratase |
| BLLs | Blood Lead Levels |
| CDC | The United States Centers for Disease |
| CNS | Central Nervous System |
| FH | Flux Healing Method |
| g | Gram |
| kg | Kilogram |
| min | Minute |
| mg/dL | Microgram of lead per deciliter of blood |
| mg/m ³ | Milligram per cubic meter |
| mL | Milliliter |
| NIOSH | National Institute for Occupational Safety and Health Hygienists |
| OSHA | Occupational Safety and Health Administration |
| PEL | Eight-Hour Average Permissible Exposure Limit |
| PM | Particulates Matter |
| U.S.EPA | The United States Environmental Protection Agency |
| RI | Refractive Index |
| SG | Specific Gravity |
| TLV | Eight-Hour Average Threshold Limit Value |

CHAPTER I

INTRODUCTION

1.1 General Statement

Thailand has been recognized as one of the most important centers of gem production and trade. This was initiated by discovery and mining of gem corundum in the country; subsequently, it has been the most famous gem for Thai customers and trading throughout the world. The Corundum family, which includes ruby and sapphire, was mined firstly in Chanthaburi and Trat provinces during the reign of King Chulalongkorn (Rama V). Subsequently, more deposits were discovered in the west and north of the country (e.g., Kanchanaburi, Phare, Lampang, Petchabun, Unbonratchathani and Sri Sa Ket) (Vichit, 1992). In the past, these natural resources were mined by manually. Afterwards, they were mined using big scale machinery. Consequently, reserves have been diminished. Thai traders now import raw materials from all over the world, particularly from East Africa. However, high gem-quality materials from East Africa are very rare. Thai craftsmen have improved their skills in cutting, polishing and treating gems over time. As a result, Thailand is now known as the world capital of colored stones.

Gem enhancement techniques in particular have been developed and handed down within the families of professionals. Each family has its own secret technique developed through practical experience, knowledge and wisdom. Most of the gem enhancements in Thailand involve heat treatment which is acceptable in the world market. However, some techniques have yet to be disclosed to the trade. The evolution of heating techniques in Thailand began with indigenous people's observation of gemstones in fire. They noticed the heat made the gems clearer and more beautiful. From this, people started studying and improving gem heating procedures. Heat treatment methods can be divided into three periods (Satukitchai, 2005).

In the first period, mangrove charcoal was used as a fuel because it gives higher temperature than other charcoals. At this stage, the heat treatment method was simple. The treater created hollow balls using indigenous red clay from the gem mine. Low quality gems were put in these balls and the hole was covered by

the same material. After that, they were heated in a brazier until the fire died out. After cooling, the gems were pounded gently. As a result, some gems improved but some were still unchanged. This heat treatment method generally can slightly increase the quality of the treated gemstones. These treated stones have been fully accepted by the worldwide markets.

The middle period started in 1972 when treaters used electric furnaces to heat treat gemstones. Unfortunately, there was no steady electricity supply in Chanthaburi province and the price of a furnace imported from Germany was very high. Therefore, there were only a few treaters who could afford this technique. At that time, the imported furnace could be operated at temperatures of 1400-1600°C. These higher temperatures gave more satisfying results. Changes in gem color from dark purple to clear pink or red that was much different from brazier changes was common. Moreover, the treaters started adding chemical agents such as borax, silica, and sodium compounds to heal fissures and cavities in the natural gems. Although, most of the treated stone using these techniques are still acceptable in the market, some specific treatments need to be disclosed as appropriate.

Since 1997, the modern period of heat treatment has been recognized due to the use of new technology. New generation treaters have more comprehensive knowledge and accumulated experience. Many instruments are both cheaper and higher in quality than before; hence, research can be done more easily. Furnace innovations are the most important development in heat treatment. Some furnaces have a channel for feeding oxygen gas into the chamber during the heat treatment process resulting in much higher temperatures than previously obtainable. Moreover, use of several chemical agents, particularly beryllium (Be) and lead (Pb) additives, are modifying the treatment method. These particular methods dealing with beryllium and lead have seriously impacted the colored stone market and they need to be fully disclosed for trading.

The addition of lead is not used for color creation but to fill the fissures and cavities of the corundum, particularly ruby (red corundum). The treatment method is not a very complicated heating process. Rubies are cleaned, trimmed or preformed into various shapes; then, they are soaked in or embedded with the lead additives and loaded into crucibles before heating (Pardieu, 2005). The ruby heat treatment method is performed according to selected parameters, especially time and temperature. Generally, the heating processes are performed using an electric furnace

for 10 to 14 hours with a maximum temperature of 900 to 1400°C (Bergman, 2005). Lead-additive, when heated, will fuse and penetrate into the fissures and cavities of the ruby. After cooling down it will turn into a glass; hence, many treaters call this lead additive, “lead-glass”. Lead-glass has a refractive index very close to ruby, therefore, it can make ruby clearer, brighter, and more beautiful (Pardieu, 2005).

Lead-glass heating techniques have actually been applied to treat diamond for some decades and it is now a very common treatment for ruby. This treatment has to be disclosed to the trade. There are many factories in Chanthaburi and Bangkok supplying lead-glass treated ruby to the market. Most gem heating factories in Chanthaburi have their own electric furnaces for lead-glass heating. Electric furnace use has been increasing because the consumable heating elements are now produced in China and are much cheaper than in the past.

In the ruby heat treatment process, the composition and amount of lead-glass, heating period and temperature are secrets to each factory. This can be problematical as the factory is usually located within the owner’s house. The problem is lead particulate matter can emit from the furnace to indoor air. Inhalation of lead particulate is the most common mode of entry of lead into the body of the treater and anyone else who lives in the house. Because lead is a toxic element, the concentration of lead in the blood is an important aspect in assessing exposure and potential adverse health effects. Long-term, even small amounts of lead exposure can cause chronic lead poisoning.

Unfortunately, no person or organization has exhibited concern about this problem that may threaten the health of these factory workers and negatively impact the environment. This is the first investigation of the concentration of lead particulate emitted from electric furnaces and the exposure of this toxic compound to people in the gemstone factories in Chanthaburi province, Thailand.

1.2 Objectives

The main objective of this study is to determine lead concentration in particulate matter emitted from electric furnaces during ruby heat-treatment processing involving lead-glass material. To this end, three sub-objectives are earmarked below.

1.2.1 To examine emission profile of lead particulate from the ruby treatment furnace.

1.2.2 To determine the exposure level of lead that may directly affect workers during the ruby treatment procedure (mixing step and opening periods) and also the effects on those living in the home factory.

1.2.3 To determine indoor lead concentration in particulate samples from different locations within the factory.

1.3 Hypotheses

1.3.1 Ruby heat treatment involving lead-glass additive causes lead contaminated particulate in the factory.

1.3.2 Lead particulate contamination appears at different levels depending on the particular process and location in the factory.

1.4 Scope of the Study

1.4.1 Sampling sites included two home factories in Chanthaburi where the treaters used lead-glass additive for heat treatment of ruby, later called Factory A and Factory B, and two residential homes where the treatment has never been conducted.

1.4.2 The respirable particulate will be collected by personal air sampler (Gilian, GilAir-5).

CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEWS

2.1. Ruby

Ruby is a red gemstone which is a precious red variety of corundum family. Corundum is an oxide mineral, chemically characterized by colorless Al_2O_3 ; however, its color varieties (e.g., red, orange, blue, yellow, green and purple) presenting in the nature are caused by impurities (e.g., Cr, Fe and Ti) and point defect in its crystal structure. The other color varieties of corundum are mostly called sapphire. Ruby means red, and is derived from the Latin *ruber* (red) through the late form *rubinus* (Hughes, 1997). For thousands of years, ruby has been considered as one of the most valuable gemstones on the earth. It has everything a precious stone should have including magnificent color, excellent hardness and outstanding brilliance. In addition to that, it is an extremely rare gemstone, especially in its finer qualities.

2.1.1 Chemical Composition and Structure

Ruby is mainly composed of aluminum (Al) and oxygen (O) forming the corundum structure of aluminum oxide (Al_2O_3) (Figure 2.1). Pure corundum is colorless; however, its pure phase rarely occurs in the nature. Colored corundum is formed by the substitution of trace metal ions into the lattice structure. Chemically, corundum is an oxide, meaning a naturally occurring mineral compound in which oxygen is combined with one or more metals. Red colored corundum, known as ruby, is a result of the presence of chromium (about 1% of Al^{3+} ions) enters the corundum lattice in the form of a trivalent ion, Cr^{3+} , isomorphously replacing some of the aluminum ions (Achiwawanich, 2007).

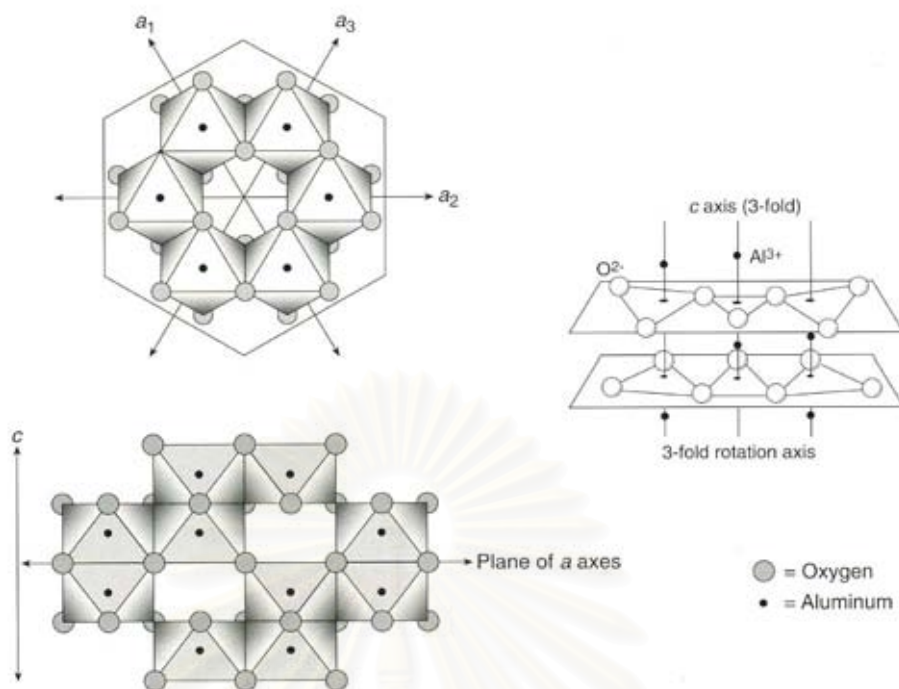


Figure 2.1 Three different views of the structure of corundum, the top illustration shows the looking down the c axis, while below is a view perpendicular to the c axis. At right is a perspective view (from Hughes, 1997).

2.1.2 Properties

Corundum is the most durable among all of gemstones. With a hardness surpassed only by diamond, and an absence of easy cleavage, corundum is very resistant to scratching and corrosion. This is borne out by the fact that most gem corundum is covered from alluvial deposits where, despite eons of weathering, crystals still display much of their original shapes. The properties of ruby can be classified into three aspects including physical, chemical and optical properties.

2.1.2.1 Physical Properties

The physical properties are concern of durability of the corundum that includes cleavage, parting, fracture and hardness. Cleavage, parting and fracture that involve a crystal's reaction to external pressure or force. This is intimately related to bonding and atomic structure.

(1) Cleavage: describes the tendency of a single crystal to break along atomic planes. As atomic planes form crystal face. It is described according to the following factor.

- The face it parallels (rhombohedron, pinacoid, etc.)
- Smoothness of the cleavage surface (perfect, imperfect)
- Ease with which the break is effected (easy, difficult)

Rhombohedral cleavage was detected more often, and the surfaces were also larger, while the prismatic cleavage steps were deeper and visible to the naked eye. At times, both rhombohedral and prismatic cleavages formed simultaneously, giving macro-steplike relief to cleaved surface.

(2) Parting: The end-result of parting is identical to cleavage-splitting along a plane of weakness. Like cleavage, this tends to produce a distinctive, step-like fracture surface. However, parting is due to structural defects, rather than the basic structure design, as with cleavage. Thus, the number of possible partings is limited to the number of defective planes present. A useful analogy is to imagine a house struck by an earthquake. If the house collapses due to a faulty architectural design, this is cleavage. But if it collapses because the builders did not follow the architect's drawings properly, it is parting.

(3) Fracture: When broken along directions other than cleavage or parting planes, corundum exhibits a conchoidal ('shell-like') to sub-conchoidal fracture. In terms of tenacity, ruby is relatively brittle, although much less so than other species, such as spinel or zircon.

(4) Hardness: The resistance that a smooth surface of a mineral offers to scratching is its *hardness*. The classic scale of hardness for minerals was developed by Frederick Mohs in 1824 and is still in use today. Corundum is nine on this scale, and, among naturally-occurring minerals, is surpassed only by diamond.

2.1.2.2 Chemical Properties

Chemical composition of ruby (Al_2O_3) leads to some properties such as melting, boiling, solubility density and specific gravity that are characteristics of ruby and other corundum varieties.

(1) Melting and boiling points: According to Belyaev (1980), the melting point of corundum is 2030°C , but other references give 2050°C . Belyaev gives corundum's boiling temperature as 3500°C .

(2) Solubility: Corundum dissolves slowly in boiling nitric acid and in orthophosphoric acid to 300°C, while dissolving well in borax at 800 to 1000°C, and in potassium bisulfate at 400 to 600°C.

(3) Density and specific gravity: are essentially synonymous, but there is a difference. Density describes the weight of a specific volume of material (usually g/cm^3), while specific gravity (SG) is a ratio comparing the weight of a substance to the weight of an equal volume of water at 4°C. Thus specific gravity has no units. Water has a SG of 1.0 (unity) and is the medium of comparison. A material with an SG of 4.0 would weight four times more than an equal volume of water. Corundum's density is usually given as 3.98 g/cm^3 .

2.1.2.3 Optical Properties

The beauty of precious stones is largely related to visual phenomena—the way in which they affect light. Light returned to the eye is reflected, while that which bends passing through a material is refracted. Selective absorption of white light results in color. These are but a few of the optical properties that affect the appearance of gems.

(1) Refractive index: Ruby has two indices of refraction because a single light ray is split into two light rays which travel at different velocities when entering the stone. The extraordinary ray, a beam of light that varies in wavelength, enters ruby with an index of refraction of 1.762. The ordinary ray, a beam of light that doesn't vary in wavelength, enters ruby with an index of refraction of 1.770. Materials with two indices of refraction are called birefringent (Chang, 2007).

(2) Luster: is the quality and quantity of light reflected by a gem's surfaces, both external and internal. Internal luster is termed brilliance, while surface luster is simply called luster.

Surface luster depends upon the stone's refractive index, polish quality and surface cleanliness (which determine the amount of light that can be reflected).

There are three major factors that affect surface luster:

- Polish quality: The better the polish the better the surface reflections, and thus, luster. Similarly, the cleaner the surface, the better the luster.

- RI: Determines the amount of reflection at the surface. The greater RI difference between air and the gem leads to the greater reflection. High gem RIs yield higher luster.
- Surface cleanliness: Dirt distorts reflections. Oils also lower the RI difference between air and gem, thus lowering luster.

Corundum displays a surface luster which is greater than glass (vitreous), but less than diamond (adamantine), and so is described as vitreous to sub-adamantine.

Internal Luster or Brilliance is the quality and quantity of light returned to the eye from reflections within the gem. There are four main factors which affect brilliance:

- Polish and surface cleanliness: The higher the polish the better the surface reflections (luster). Similarly, the cleaner the surface, the better the luster.
- RI: Determines the size of the critical angle, which in turn influences the amount of light returned from pavilion facets.
- Transparency (clarity): Affects light transmission, which influences brilliance.
- Proportions: These strongly influence the amount of light returned (via total internal reflection) or lost (via unplanned leakage).

2.2. Ruby Enhancement

For over two thousand years rubies have been heated to enhance their reddish-pink color, and remove bluish hues. Heat treatment was accomplished using simple tools, such as a blow-pipe in Figure 2.2(a) and charcoal burner in Figure 2.2(b).



Figure 2.2 (a) The centuries old technique of blow-pipe heat treatment of ruby in Sri Lanka (b) Primitive charcoal oven at Chathaburi town, Thailand (from Hughes, 1997).

Today, heat treatment of ruby is carried out using a combination of chemicals such as beryllium, borax, lead, and tantalum. One telltale sign of heat treatment is the presence of small discoid fractures that appear around natural mineral inclusions. Occasionally, the stress of the heat treatment used to enhance color will create fractures (“decrepitation feathers”) which must then be repaired. A high percentage of rubies in the market have been either heat treated, flux-healed or both. Small surface fractures are sometimes filled with a detectable process known as “glass-infilling”. According to the American Gemological Laboratories (AGL), 70 percent of Mong Hsu Burma rubies have been flux-healed or fracture-filled, with the work usually being conducted in Thailand. Thai mines in Chanthaburi and Kanchanaburi still produce small quantities of ruby, but most material coming from Thailand these days originated elsewhere (KHI Inc., 2007).

2.2.1 Flux-Healing Method

Gemstones evolve from a liquefied hot “molten soup” of melted rock. As this piping hot material cools, outside matter becomes trapped inside and the growth process of a gemstones being. These trapped materials in the host may be solid mineral, liquid or gas and become defects in the gemstone.

Guest crystal, the presence of calcite, mica, and other solid mineral inclusions in ruby may affect the clarity of the stone. The presence of rutile in the form of silk may reduce the transparency of the stone; the silk can be partially of

totally “removed” via thermal treatment though in other cases the silk may actually contribute to the development of color.

Liquid, depending on the genetic characteristics of the corundum, liquid may be present in several configurations such as entrapped internally in the host (primary) and entered the host through surface-reaching fissures (secondary). The liquid may become incorporated with other guest crystals and inclusions forming interesting and often unique patterns. In time, the liquid may be “healed” forming “fingerprints” and other patterns (Themelis, 2004).

The fissures, we see in untreated ruby is due to an unequal expansibility rate of the host at the cooling stage. Developed without specific pattern or structural arrangement they may be entrapped within the host or alternatively reach the surface of the host. Internal fissures can be empty voids, or they may contain guest minerals, liquids, or gases. Surface-reaching fissure may be empty voids or could just as easily contain guest minerals. Surface-reaching depressions are known as “cavities”. Figure 2.3 shows some typical clarity imperfections in ruby.

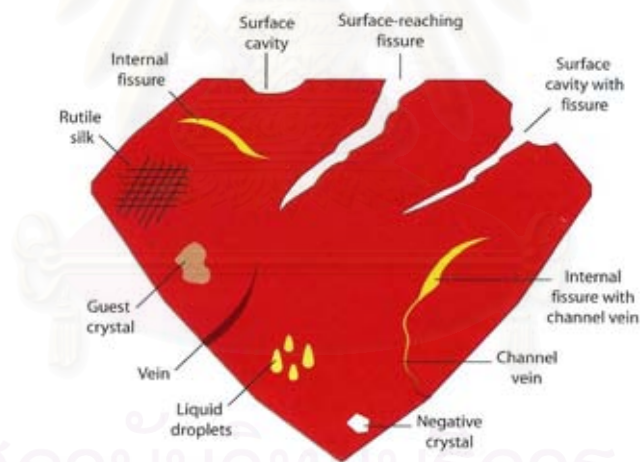


Figure 2.3 Diagram showing some typical clarity imperfections in ruby (from Themelis, 2004).

Surface cavities, fracture, or fissure in ruby can be repaired using the “flux healing” (FH) method. The flux-healing process involves exposing the stone to a combination of heat and solvents (borax and/or other fluxes) to fill any voids with molten low-viscosity flux “glass”. As the flux mixture fills a fracture, it dissolves the walls of the fracture until the liquid in the crack becomes saturated with molten corundum/ruby solution.

The mechanism of flux-healing of a fracture in corundum can be explained following (Figure 2.4) (Hughes, 2001):

- A. Open fracture and/or fissure, unhealed.
- B. During heat treatment, flux enters the fracture and dissolves the walls of the crack.
- C. During cooling, dissolved corundum recrystallizes in the crack, thus healing it closed. The newly crystallized ruby is essentially a synthetic ruby grown in the crack alone. It contains small pockets of now-solidified flux glass, along with some trapped gas pockets. For purposes of this diagram, the surrounding natural ruby and the synthetic ruby in the crack are shown in two different colors. In reality, no distinction can be seen between the surrounding natural ruby and the newly grown synthetic ruby.
- D. Any flux glass present on the surface can be dissolved away with acid. The synthetic ruby in the crack is unaffected by the acid, as is the ruby as a whole.

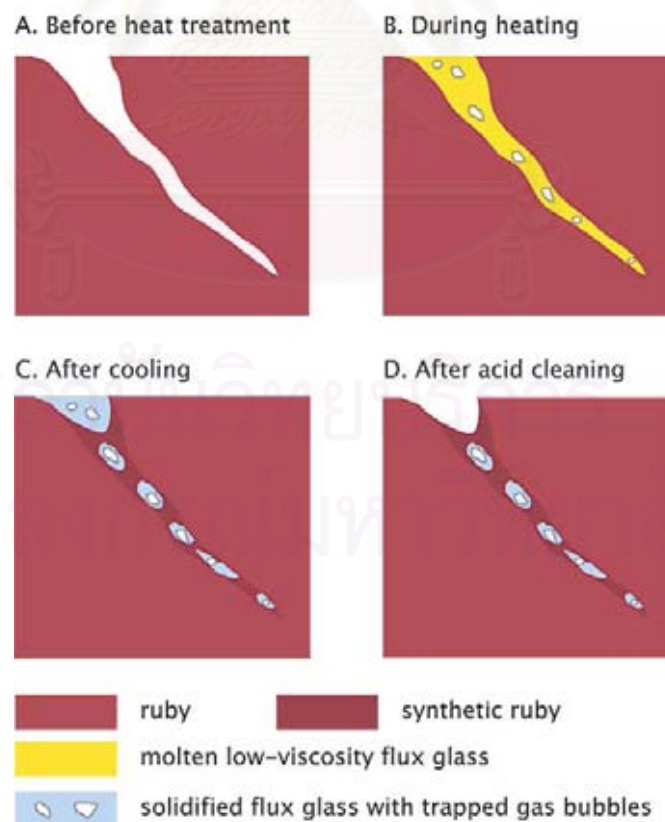


Figure 2.4 Diagram of a flux-healed fracture (from Hughes, 2001).

When the molten flux mixture cools, the synthetic corundum will permanently fuse the crack together, but the process will leave behind small air pockets surrounded by solidified glass. These telltale signs are the characteristic signature of the healing process. A filled fracture is much less visible because the filler replaces air (RI = 1.00) with a substance which has an RI that more closely matches the gem itself (1.76–1.77). Flux-Healing of fractures will reduce internal reflections making the ruby appear more transparent while permanently fusing the fracture together, making the ruby more durable.

2.2.2 Lead-Glass Healing Method in Chanthaburi, Thailand

The most popular fracture healing in Chanthaburi is done using lead-glass. The treater applies lead-glass to heal the cavities of the ruby. Some terminology problems may occur with this treatment regarding the “lead-glass” definition as many different formulas have been used in the process. For example, pure lead oxide, lead oxides mixed with silica or fluxes like borax have been used, Lead compounds actually effect the environment and impact on the health of the treater. Hence, details of this method were studied.

The methodology applied in the lead-filled treatment of ruby is simple and effective. Schematic diagram of ruby treatment is presented in Figure 2.5. First, rubies are cleaned, trimmed or preformed into various shapes; then, they are mixed with the lead-glass additives (mixing step) and loaded into a crucible before heating.

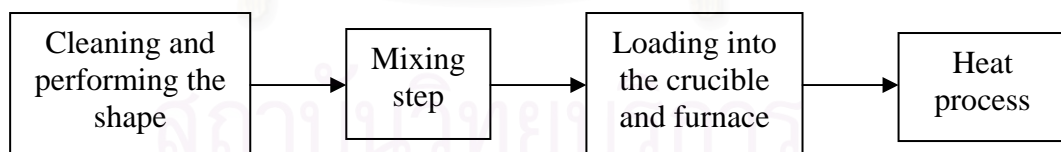


Figure 2.5 Schematic diagram of lead-filled treatment.

The treatment parameters involved in the process (e.g., lead additive furnace, and heating process) are described below.

(1) Lead-glass additive: These formulae are top secret for each ruby heat treatment factory. The treaters keep the recipe within their family. However, Pardieu (2005) has reported that “lead-glass” with many different formulas can be used in the process. Consequently, the results can be very different. Themelis (2004) has suggested it is likely that a wide variety of chemical additives are used in the

treatment of ruby. The substances used in Thailand as additives in the treatment are actually agricultural chemicals. The main chemical used in lead-glass additives (Themelis, 2004) can be summarized below:

- Lead (II) oxide (PbO – CAS# 1317-36-8): A melting point of 888°C , the fluxing, and refractive properties valued of lead (II) oxide also make it attractive for heat treatment of ruby.
- Aluminum Oxide (Al_2O_3 – CAS# 1344-28-1): Pure aluminium oxide or alumina (99.999%) has been used to compensate the amount lost by dissolution of the ruby when fluxes are used in the heating process.
- Sodium tetraborate deca-hydrate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ – CAS# 1303-96-4): This chemical is commonly known as borax, and it is by far the most widely used flux in heating ruby. A white, powdery, monoclinic crystalline salt, with a melting point of 741°C and is soluble in water.
- Quartz: Crushed white, opaque, natural crystalline-type quartz (SiO_2) mixed with borax and other additives are used routinely in the filling process of ruby
- Distilled water (H_2O – CAS# 7732-18-5): An essential compound used in the mixing of fluxes.

These additives are mixed in a certain ratio and placed in a container. A small amount of distilled water is added to the cup forming a slurry mixture rather like paint. The rubies are soaked or embedded in the lead glass additives and loaded in a crucible (Figure 2.6 (a) and (b)); the heat process is performed according to selected heating parameters (including time and temperature).

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Figure 2.6 (a) Ruby soaked with lead-glass additives (b) Loading ruby mixed with lead-glass additives into crucibles.

(2) The furnace: in Chanthaburi Province, Eastern Thailand, ruby is heat treated with chemicals using high temperature electric furnace (Figure 2.7).



Figure 2.7 Electric furnace used in Chathaburi province, Thailand.

(3) Heat Treatment Process: Figure 2.8 shows time and temperature for lead-glass filled process. In heat-up, the temperature is usually set around 200°C per hour. Soaking period is depending upon size of ruby, type of additive, operating temperature, etc. Typically, the treatment processing time is performed at about 5 to 6 hours (Bergman, 2005).

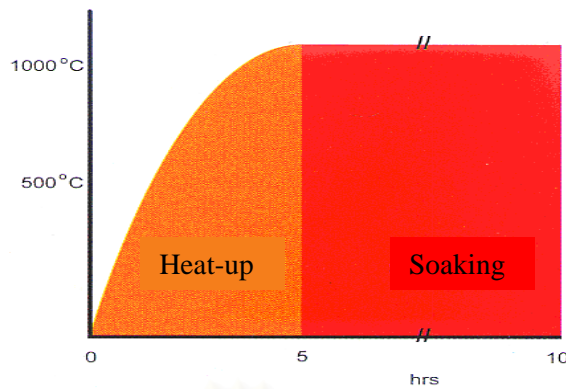


Figure 2.8 Heat treatment condition of ruby involving lead-glass compound (adapted from Themelis, 2003).

The process starts with pre-forming the ruby rough to remove matrix and other impurities. After the first heating, the now bright pinkish red pre-forms are packed in a crucible with the lead and silica rich oxide powders and heated from 900 to 1,000°C in atmosphere controlled electric furnaces. Some stones are heated in this way several times in order to obtain the best results (Bergman, 2005). Then, the heat treatment process was over; the simplest way to cool down the furnace is to switch-off the heat-supply. In this segment, the treater decides when the crucible should be removed from the furnace and, subsequently, when the stones should be removed from the crucible and under what conditions.

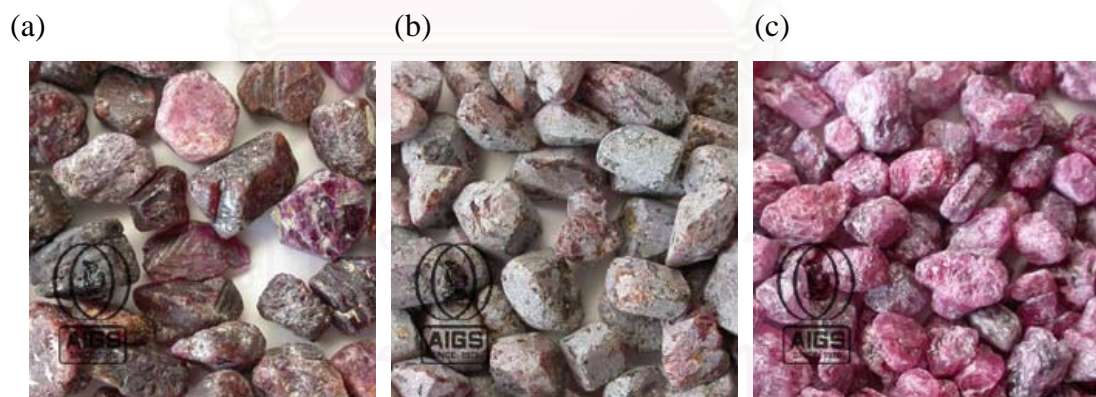


Figure 2.9 (a) Rough, (b) pre-forms, and (c) after first heating of ruby (from Bergman, 2005).

Removal of the ruby from the crucible requires experience and skill because ruby is often “glued” to each other or to the crucible by fusion, requiring mechanical removal or even breakage of the crucible. Ruby is then cleaned with acids

to remove any flux or additives remnants or is simply preformed ready for subsequent cutting/polishing process (Themelis, 2004).



Figure 2.10 (a) Removal of the ruby from the crucible (b) Glued ruby after lead-glass filled heat treatment.

2.3 Air Pollution from Ruby Enhancement Process

This enhancement process not only creates more beautiful ruby but also generates air pollution in the form of heat, particulates, and lead within the factory. There are several steps of enhancement method that generate air pollution (Figure 2.11).

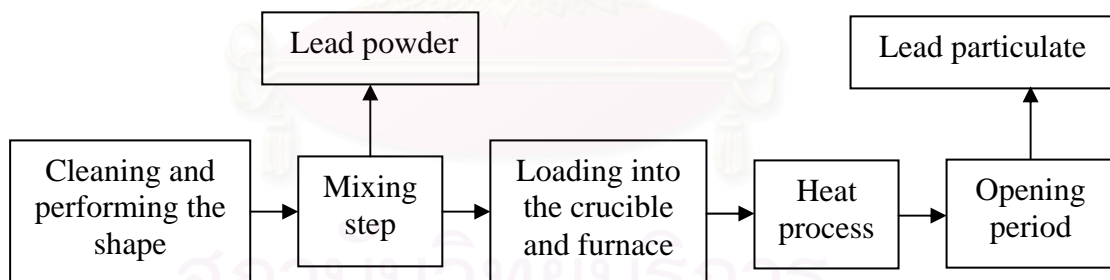


Figure 2.11 Air pollution generated from ruby enhancement process.

After cleaning and performing, rubies are soaked with the slurry of lead-glass additive. Normally, this mixing step takes not more than 5 min. However, before adding distilled water the lead-glass additive is a fine powder and it can spread easily into the air. Therefore the treater can be exposed to lead in this step. When soaked ruby are placed into the furnace, lead is heated in an oxidizing atmosphere with the maximum temperature not higher than the boiling point (1472°C). Subsequently, lead is in the oxide form (Abel, 1975) which is solid. Normally, it will accumulate as fine particulate, a byproduct of heat treatment process (Pacyna, 1987;

Barton et al., 1990; Seeker, 1990; Hertberg et al., 1992). When the treater opens the gate of the furnace lead particulate can emit into the atmosphere and expose the treater.

2.4 Particulates Matter (PM)

2.4.1 Definition

Particulate matter (PM) is an air pollutant consisting of a mixture of particles that can be solid, liquid or both, are suspended in the air and represent a complex mixture of organic and inorganic substances. These particles vary in size, composition and origin. Their properties are summarized according to their aerodynamic diameter, called particle size (Krzyzanowski, 2005).

- The coarse fraction is called PM₁₀ (particles with an aerodynamic diameter smaller than 10 μm), which may reach the upper part of the airways and lung.
- Smaller or fine particles are called PM_{2.5} (with an aerodynamic diameter smaller than 2.5 μm); these are more dangerous because they penetrate more deeply into the lung and may reach the alveolar region.

The size of the particles also determines the time they spend in the atmosphere. While sedimentation and precipitation remove PM₁₀ from the atmosphere within a few hours of emission, they are usually thought of as “settable”, PM_{2.5} may remain for days or even a few weeks. Those of smaller diameter are referred to as “suspended” (Warner, 1937).

2.4.2 Size of Particulates Matter

Suspended particles vary in size, composition and origin. It is convenient to classify particles by their aerodynamic properties because: (1) they govern the transport and removal of particles from the air; (2) they also govern their deposition within the respiratory system; and (3) they are associated with the chemical composition and sources of particles. These properties are conveniently summarized by the aerodynamic diameter that is the size of a unit-density sphere with the same

aerodynamic characteristics. Particles are sampled and described on the basis of their aerodynamic diameter, usually called simply the particle size (WHO, 2000).

Defining particle size for spherical particles is easy; it is simply the diameter of the particle. For non-spherical particles, the term "diameter" does not appear to be strictly applicable. For example, what is the diameter of a flake of material or a fiber? Also, particles of identical shape can be composed of quite different chemical compounds and, therefore, have different densities. The differences in shape and density could introduce considerable confusion in defining particle size.

In air pollution control, it is necessary to use a particle size definition that directly relates to how the particle behaves in a fluid such as air. The term "aerodynamic diameter" has been developed by aerosol physicists in order to provide a simple means of categorizing the sizes of particles having different shapes and densities with a single dimension. The aerodynamic diameter is the diameter of a spherical particle having a density of 1 g/cm^3 that has the same inertial properties in the gas as the particle of interest. The aerodynamic diameter for all particles greater than 0.5 micrometer can be approximated using the following equation.

$$d_{pa} = d_{ps} \sqrt{P_p} \dots \dots \dots (2.1)$$

where d_{pa} = Aerodynamic particle diameter, μm
 d_{ps} = Stokes diameter, μm
 P_p = Particle density, g/cm^3

Particle density affects the motion of a particle through a fluid and is taken into account in Equation 2.1. The Stokes diameter for a particle is the diameter of the sphere that has the same density and settling velocity as the particle. It is based on the aerodynamic drag force caused by the difference in velocity of the particle and the surrounding fluid. For smooth, spherical particles, the Stokes diameter is identical to the physical or actual diameter.

Inertial sampling devices such as cascade impactors are used for particle sizing. These sampling devices determine the aerodynamic diameter. The term "aerodynamic diameter" is useful for all particles including fibers and particle clusters. It is not a true size because "non-spherical" particles require more than one dimension to characterize their size. The terms PM10 and PM2.5 also use the aerodynamic diameter formats (U.S. EPA, 2008).

Various different fractions are chosen when it comes to making the actual measurements. Thus Total suspended particles (TSP) refers to the fraction

measured by a high volume sampler widely used and corresponds roughly to diameters up to $\sim 45\mu\text{m}$ (but varying according to wind speed and orientation). More recent methods are designed to measure particles in specific size ranges- thus PM10 and PM2.5 refer to the samples collected in samplers with $10\mu\text{m}$ and $2.5\mu\text{m}$ upper cut offs respectively. Particulates can also be classified according to the extent to which they penetrate the respiratory system. It is generally thought that the upper cut-off point for particles to be deposited in the windpipe or large airways of the lungs (i.e. thoracic particles) is $\sim 10\mu\text{m}$, and $\sim 2.5\mu\text{m}$ and below for those penetrating deeper into the gas-exchanging regions (respirable particles) (POST, 1996).

The heat treatment of ruby emits lead particulates into indoor air. They tend to remain entrained in air stream. Such particulate is referred to as “suspended particulate”. Since this class of air contaminant dust is respirable, it is certainly more harmful to man than the larger-diameter settleable particulate (Warner, 1937). Collection of suspended particles from the air by filtration is by far the most popular technique, particularly when no breakdown of the sampled particles distribution by size is desired.

2.4.3 Routes of Human Exposure

Particulate pollutants enter the human body almost exclusively by way of the respiratory system and their most important immediately effects involve this system. The intensity of these effects depends on the degree of particulate penetration within the system, and the particulate toxicity (Stoker and Seager, 1976).

2.4.4 Human Health Adverse Effects

The extent of penetration into the respiratory tract is generally accepted to be a function of particulate size. This dependence is a result of anatomical characteristics of the human respiratory system which is represented in Figure 2.12. The respiratory tract is often classified into an upper tract (the nasal cavity, pharynx, and trachea) and a lower tract (the bronchi and lungs).

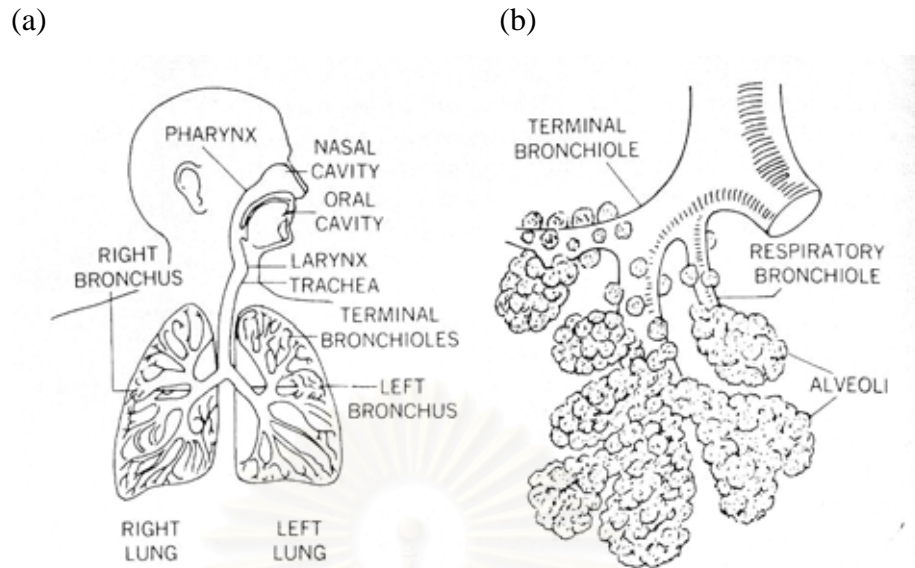


Figure 2.12 (a) The major anatomical features of the human respiratory tract (b) The terminal bronchial alveolar structure of the human lung (from Stoker and Seager, 1976).

In the upper respiratory tract particles greater than $5.0\ \mu\text{m}$ in diameter are filtered from inhaled air. Hairs in the nasal passage form the first line of defense, but particles may also be trapped in the mucous which lines the nasal cavity and trachea. Particles smaller than $5.0\ \mu\text{m}$ in diameter may escape the defense mechanisms of the upper respiratory tract and enter the lungs. Those in the size range 0.5 to $5.0\ \mu\text{m}$ may be deposited as far as the bronchioles, but few reach the alveoli. While particles less than $0.5\ \mu\text{m}$ in diameter reach and may settle in the alveoli.

Particulate matter that enters and remains in the lungs can exert a toxic effect in three different ways:

(1) Particles that are themselves inert may interfere with clearance mechanisms in the respiratory tract and prevent or slow the removal of other harmful particles. Observed physiological responses related to this effect include a slowing of ciliary beat and mucous flow in the bronchial tree.

(2) The particles may carry adsorbed or absorbed irritating gas molecules and thus enable such molecules to reach and remain in sensitive areas of the lungs. The process of sorption takes place when an individual molecule impacts on the surface of a particulate and does not rebound, but sticks or sorbs.

(3) Particulates may be intrinsically toxic and, as a result, directly affect the body. Specific concern has been expressed about a number of trace metals.

It is a well-established fact that many such metals are found among the airborne particles derived from high temperature combustion sources. Many of these metals preferentially sorb onto small particles of the type that are most difficult to remove with conventional control equipment, and which present the greatest hazard through inhalation. Eight metals found in the air are considered to be toxic. They are nickel, beryllium, cadmium, tin, antimony, lead, bismuth, and mercury (Stoker and Seager, 1976).

2.5 Lead

2.5.1 Chemical and Physical Properties

Lead has atom number 82 and is a bluish-gray metal of bright luster. It is soft, malleable, ductile, a poor conductor of electricity, and very resistant to corrosion. Lead belongs to group IV-A of the periodic table, has an atomic weight of 207.2, a melting point of 328°C, and specific gravity of 11.4 g/cm³. It occurs in two oxidation states, II and IV. In most inorganic compounds, it is in the II oxidation state. There are four stable isotopes, ²⁰⁴Pb, ²⁰⁶Pb, ²⁰⁷Pb and ²⁰⁸Pb with relative abundances of 1.48, 23.6, 22.6 and 52.3%. Two radioactive isotopes are used as tracers (²¹⁰Pb, t_{1/2} = 11 h, and ²¹²Pb, t_{1/2} = 10 h). Chloride and bromide salts are slightly soluble in water, whereas carbonate and hydroxide salts are almost insoluble (Bradl, 2005).

2.5.2 Lead from High Temperature Processes

There are many papers reviewed about the behavior of lead emitted from various high temperature processes such as power generation, waste incineration, boilers, and etc.

Hertzberg (1992) studied metal dust from combustion process, the result illustrated that the range diameters of lead dusts particles are 20 to 60 μm. Carroll (1994) evaluated the fate of trace metals emission from incinerator. He found that volatile metals (lead, arsenic, cadmium, etc.) tend to enrich in the fine particulate fractions, increasingly so with increased volatility. Seeker (1990) and Barton et al. (1990) suggested that in combustion system, lead and other trace metals generally volatilize in the flame zone, react, and then (with the exception of mercury) become

supersaturated in the cooling gas stream, condense and nucleate to form a metal aerosol.

Pacyna (1987) reported that combustion temperature in boilers, furnace, roasters, etc. is the key parameter affecting the amount of lead released into the atmosphere, as well as their chemical form and particles size distribution. The metallic lead and its oxides and sulphide are commonly found in stack dust. Sofilić (2004) also mentioned that the presence of lead in steel mill electric-arc furnace dust in the form of PbO phase, i.e. $PbSO_3/PbSO_4$ forms.

2.5.3 Routes of Human Exposure

It is important to understand the ways that lead can get into the body. This is referred to as routes of exposure. With lead, there are two main routes of exposure: inhalation and ingestion (TFHRC, 2007).

2.5.3.1 Inhalation

This is by far the most important exposure route in construction. Lead may be in the air if dust is created by grinding or similar procedures, or if fumes are created by welding torches. High levels of lead may be present yet not be visible to the naked eye. This airborne material is easily breathed in by any workers in the vicinity. Once inhaled, air follows a pathway from the nose to the windpipe, and then travels to the lungs.

2.5.3.2 Ingestion

Ingestion exposures can happen on the job in surprising ways. Many cases have been documented where workers consumed significant amounts of lead because they handled food and cigarettes before they washed the lead dust off their hands and clothes. This pathway also is a major problem for small children. Children sometimes swallow interior paint chips, which have a slightly sweet taste. Because of this problem, lead paint for use on interior surfaces and toys has been banned for many years.

2.5.4 Human Health Adverse Effects

Lead is a very toxic substance affecting a variety of target organs and systems including the brain and the nervous, renal, reproductive, and cardiovascular systems. Effects are dose dependent. They may be acute (clinically obvious) or chronic (typically symptoms/effects are not easily diagnosed).

2.5.4.1 Acute Effect

Acute exposure, with Blood Lead Levels (BLLs) >60 mg/dL, may produce colic, shock, severe anemia, nervousness, kidney damage, irreversible brain damage, and even death. Acute responses may differ in adults and children since children under age five are more vulnerable to the neurotoxic effects of lead (Godish, 2003).

2.5.4.2 Chronic Effect

Since lead accumulates and is only slowly removed from the body, repeated exposures (over months to years) commonly results in elevated BLLs. Since it is stored in bone, BLLs reflect relatively recent exposures (past 1 to 3 months) and mobilization from bone and other depots. Though not indicative of the total body burden, blood lead is relatively closely correlated with exposure levels.

Hematological change i.e. effected on blood chemistry and associated physiological changes are the earliest manifestations of chronic exposure. Lead interferes with the synthesis of heme (the O_2 -carrying component if Hb in red blood cells). Inhibition of enzymes involved in heme synthesis has been observed at BLLs as low as 10 $\mu\text{g/dL}$ while 30 $\mu\text{g/dL}$ of BLLs in adults and as low as 12 $\mu\text{g/dL}$ in children inhibits of vitamin D production.

Lead exposures may cause adverse sexual and reproductive effects. Sperm abnormalities, reduce fertility, and alter testicular function have been observed in male industrial workers at BLLs of 40 to 50 $\mu\text{g/dL}$.

The nervous system is adversely affected by lead. At high blood levels (>80 $\mu\text{g/dL}$), it cause encephalopathy (brain damage). There is evidence to suggest that lead may impair peripheral nerve conduction in children at BLLs as low as 20 to 30 $\mu\text{g/dL}$. Brain wave changes have been observed at level as low as 15 $\mu\text{g/dL}$.

Prospective epidemiological studies have shown an association between general measures of intelligence (intelligence quotient, IQ) in children and pre- and post- natal blood levels as low as 10 to 15 $\mu\text{g}/\text{dL}$. Young children (<7 years old) exposure to relatively low lead levels (10 to 40 $\mu\text{g}/\text{dL}$) may results in neurodevelopment effect: decreased intelligence, short-term memory loss, reading and spelling underachievement, impairment of visual motor function, poor perception integration, disruptive classroom behavior, and impaired reaction time. As a consequence, the U.S. Centers for Disease (CDC) has issued a guideline value of 10 $\mu\text{g}/\text{dL}$ as the lowest BLL of public health concern in children (Godish, 2003).

In addition, lead is a potential carcinogen. It can cause mutations and cell transformation and interfere with DNA synthesis in mammalian cell cultures. Animal studies have shown that it can induce kidney tumors. Though not definitive, epidemiological studies suggest a causal relationship between lead exposure and cancer. Based on this evidence, USEPA has identified lead as a Group 2B human carcinogen (carcinogenicity has been confirmed in animal studies; human studies are inconclusive) (Godish, 2000).

Acute and chronic exposure response associated with different BLLs in children and adults are summarized in Table 2.1.

Table 2.1 Blood Lead Levels and associated health and physiological effects in children and adults (from CDC, Preventing Lead Poisoning in Children, DDHS, Washington, D.C., October 1991.).

| BLLs (µg/dL) | Children | Adults |
|---------------------|--|---|
| <10 | | Early signs of hypertension, ALA-D inhibition |
| 10-15 | Crosses placenia, Neurodevelopmental effects, ALA-D inhibition, Impairment of IQ, Increase erythrocyte - protoporphyrin, Reduce gestational age and birth weight | |
| 15-20 | | Increased erythrocyte protoporphyrin |
| 20-30 | Altered CNS electrophysical response, Interference with vitamin D metabolism | |
| 30-40 | Reduced Hb synthesis, Peripheral neuropathies | Systolic hypertension |
| 40-50 | | Reduced Hb synthesis |
| 60 | Peripheral neuropathies | Reproductive effects in females |
| 70 | Anemia | |
| 80 | | Anemia, Encephalopathy symptoms |
| 80-100 | Encephalopathy symptoms, Chronic nephropathy Colic and other gastrointestinal symptoms | |

Note: CNS = central nervous system, ALA-D = aminolevulinic acid dehydratase

2.5.5 Occupational Health Standard for Lead

Table 2.2 presents the occupational health standard for lead as recommended by the Occupational Safety and Health Administration (OSHA), National Institute for Occupational Safety and Health (NIOSH), and the American Conference of Governmental Industrial Hygienists (ACGIH)

Table 2.2 OSHA, NIOSH and ACGIH occupational health standards for lead.

| Constituent | Standard level (mg/m ³) | |
|-------------|-------------------------------------|------------------------------------|
| | PEL (OSHA) ¹ | TLV (NIOSH and ACGIH) ¹ |
| Lead | 0.05 | 0.05 |

From: ¹ U.S.EPA, 1997

Note: PEL = Eight-Hour Average Permissible Exposure Limit
TLV = Eight-Hour Average Threshold Limit Value

The Notification of the Ministry of Interior B.E. 2520 (1997) under the section of "The Workplace Safety & Environmental (Chemical Material)" recommended standard for lead and its inorganic compounds as follows:

Table 2.3 Thailand occupational health standards for lead.

| Constituent | Average concentration throughout working period(mg/m ³) ¹ |
|----------------------------------|--|
| Lead and its inorganic compounds | 0.2 |

From: ¹ SHE, 1997

2.5.6 Ambient Air Quality Standard for Lead

Pollution Control Department (PCD), Ministry of Natural Resource and Environment, Thailand and U.S. Environmental Protection Agency (U.S.EPA) has set ambient air quality standards for lead following:

Table 2.4 Ambient Air Quality Standard for Lead.

| Ambient air quality standard | Averaging time | Level (mg/m ³) |
|--|-------------------|----------------------------|
| Thai ¹ | 1 month | 0.0015 |
| National Ambient Air Quality Standard (NAAQS) ² | Quarterly Average | 0.0015 |

From: ¹ PCD, 1995 and ² U.S.EPA, 1990

2.6 Literature Reviews

Tosteson et al. (1982) collected respirable particulate matter during a personal monitoring study. Respirable particles were collected on Millipore's Fluoropore filter (1- μm pore diameter) using the Harvard EPRI sampling system. The particulate matters were analyzed for Fe, Al, and Pb content. The results show that Pb indoor concentration (median = 79 ng/m^3) were found to be less than both personal (median = 112 ng/m^3) and outdoor Pb concentration (median = 106 g/m^3). The indoor, outdoor, and personal levels of Fe and Al were not significantly different.

Hlavay et al. (1992) evaluated metals in respirable (<5 μm) and coarse (5-20 μm) dusts in 3 workshops in Hungary: (1) a metal processing workshop (welders, grinders and others); (2) a grave-stone polishing-cutting workshop (stonecutter, grave-stone worker, letter-cutter); (3) stove demolition workshop (stove demolition worker and other). The results show that in the metal processing workshop, the ratio of the respirable particles to the total was found to be 58% (welder), 28% (grinder) and 28% (others). Concentrations of 4 toxic metals, Cr, Co, Pb and Cd were found in dust collected at the grave-stone polishing-cutting workshop. The toxic metal content of coarse and respirable-size dusts was dependent upon the working procedure and workplace. Unfortunately; the respirable particulates definitely consisted of more toxic metals than the coarse ones. Similar results were collected at the stove demolition shop; the metals accumulated in respirable-size particulates. The worker dismantling the stoves was especially exposed to an extremely high amount of Pb. For Cr, Co and Cd, the groups working with stove demolition were exposed to a slightly higher amount than those in the other occupations.

Feng and Barratt (1994) measured Pb and Cd levels in different size fractions of indoor dust. The results shows that dusts are dominated by particulate matter <500 μm . Pb levels in office dust in the particulate fraction >75 μm are clearly shown to be higher than that in domestic dust. Generally, for domestic premises, Pb and Cd levels increase with a decrease in the particle size and with an increase in house age, while for office dust, the Pb level increase with an increase of particle size. For domestic house, most of the metals are bound to carbonate and Fe-Mn oxides in fine dust. For office dust, the situation is more complicated, with a clear increase in Pb in the organic and residue fraction in coarse dust.

Chadwick et al. (1997) investigated occupational metal exposure in thermal spraying processes. Workers were categorized into four job groups; Grit blasting (n = 1), electric arc spraying (n = 3), plasma spraying (n = 24) and detonation gun spraying (n = 6). Full-shift ambient monitoring was undertaken to determine daily 8-h time weighted average (TWA). Air samples were collected from the workers breathing zone. The results show the levels of exposure to every metal were highest in plasma prayers and, on occasion exceeded UK Occupational Exposure Limits. Exposure to metals during detonation gun and electric arc spraying was better controlled and levels remained below the relevant Occupational Exposure Limits throughout the study period. The findings clearly indicate that exposure to and uptake of metals may exceed UK Occupational Limits when spraying is performed manually or semi-automatically and where control relies on local exhaust ventilation and personal respiratory protective equipment.

Pfeifer et al. (1999) measured personal exposure to airborne metals in two groups, London taxi drivers and office workers (10 subjects per group) in July 1995 and September 1996. The results show that the mean exposure to Mn was higher among the office workers than the taxi drivers in both years. This was due to the fact that approximately half the office workers commuted via the underground railway system where airborne dust and metal concentrations are significantly elevated over those in the general environment. Similar results have been noted in other cities having underground rail system. Taxi drivers had higher exposures than office workers to Mg and Pb in both years. Commuting via the underground also had a significant impact on exposures to TSP, PM_{2.5}, Al, and Ca, but had little effect on exposures to Mn. The air in the underground was particularly rich in Mn, approximately 10 times higher than the air in the general environment. There are several possible sources for this Mn, including mechanical wear of the steel wheels on the steel rails, vaporization of metal from sparking of the third rail, or brake wear.

Molnár et al. (2005) measured personal exposure and ambient, indoor and outdoor levels of PM_{2.5} in the winter of 2003 in a Swedish residential area. Samples were collected for 24 hour. The results show wood-smoke particles made statistically significant contributions of K, Ca, and Zn for both personal exposure and indoor concentration. The median levels of these elements being 66–80% higher for the wood-burning group. In addition, Cl, Mn, Cu, Rb, and Pb were found to be possible markers of wood smoke, though levels of these were only significantly

higher among the wood-burning group for either personal exposure or indoor concentrations.

Choël et al. (2006) collected dust on air filters at a Pb-Zn refinery located in northern France. The result indicated that lead components were mainly metallic lead (Pb), lead sulfide (PbS), lead sulfates (PbSO₄, PbO·PbSO₄ and 4PbO·PbSO₄), lead oxide (PbO) and lead oxychloride (Pb₂O₂Cl₂).



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CHAPTER III

METHODOLOGY

3.1 Sampling Plan

Lead particulate samples were collected on the basis of NIOSH 7082 method (see appendix A) using personal air sampling pumps at an average flow rate of 3 L/min. Sampling plan was divided into three main parts (Figure 3.1). The description of each part is explained below.

3.1.1 Emission Profile

The objective of this sampling part was to study lead emission profile from the furnace. Personal air sampling pumps were placed above the gate of furnaces in two factories later described as Factory A and Factory B. Sampling plan was divided into two parts. The first part was a preliminary investigation of the whole heating process in Factory B. The results from this part would indicate the most appropriate step for further monitoring. Sampling periods were therefore set for several different cycles which are diagramed and detailed in the next chapter. In general, these sampling rounds include 4.5 and 5.5 hours of heating up step (A and A*), 5.5 hours of soaking step (B), 5.5 hours of soaking step plus 1 hour after gate opening and cooling down (B*), 9 hours of cooling down promptly after gate opening (C*) and 8 hours of cooling down after gate opening for one hour (C) (see also Figure 4.1). It should be noted that gate opening takes a very short time which is usually carried out immediately at the end of soaking step and then the gate is closed and the furnace will be left for continuous cooling down.

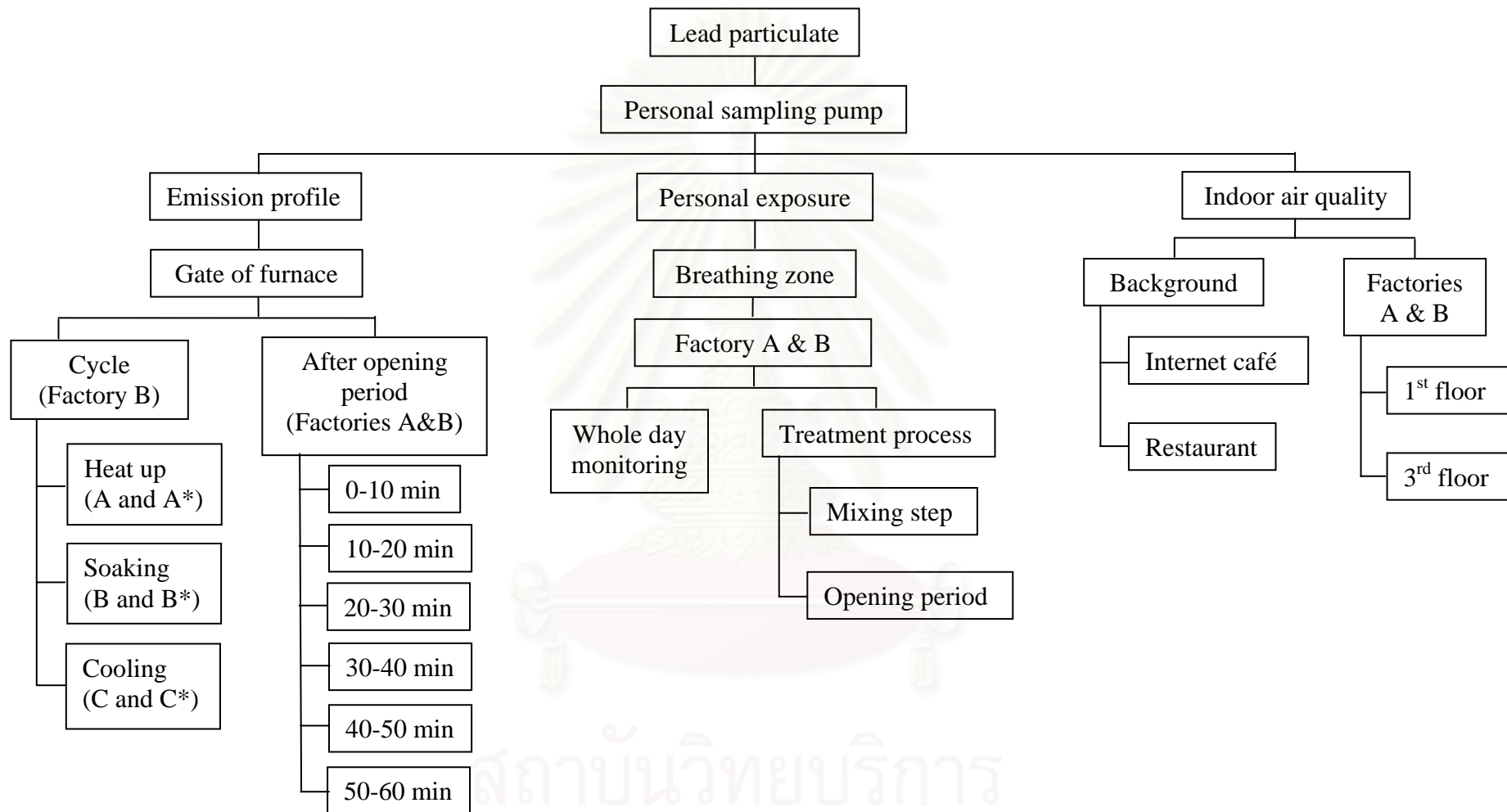


Figure 3.1 Schematic diagram of sampling plan under this thesis

The second sampling step was set up to focus on one hour after gate opening. Hence, detailed sampling was planned to collect particulate matter samples during 0-10, 10-20, 20-30, 30-40, 40-50, 50-60 minutes after gate opening at the end of soaking period and beginning of cooling down (see also Figure 4.3). Sampling sites were set up at Factories A and B to monitor the two furnaces in each factory. This part will lead to understanding lead emission profile after the gate opening.

3.1.2 Exposure of the Treater to Lead Particulate

Lead particulates collected from the breathing zone of the treaters in factories may indicate invisible harmful effects. The samples were collected during the process of ruby treatment, including mixing step and opening period in particular. In addition, monitoring of personal lead concentrations were also done but sampling times between Factories A and B were different. Factory A personal lead concentration was measured for 24 hours because the treater lives at the factory all the time. On the other hand, the treater of Factory B usually works at his office during day and stays at the home factory at night. Therefore, monitoring lead personal concentration of this factory was measured only during the time period treater was present. Subsequently, lead concentrations detected were compared with the occupational health standard for lead in the work place and ambient air quality standard. Details of this step are clarified in the next chapter.

3.1.3 Indoor Lead Particulate

To study the effect of lead-glass on the concentration of lead in indoor air, lead concentration in collected samples from Factories A and B were measured and correlated with those monitored from background stations including an internet café and restaurant. In addition, lead concentrations at different locations such as first floor and third floor within the same factory were also compared and taken into account. Details of collection and the results are reported in the next chapter.

3.2 Apparatus

3.2.1 Personal Air Sampling Pump

Personal air sampler (Gilian, GilAir-5) as shown in Figure 3.2 were used throughout this investigation because of they are economically designed for personal sampling of respirable particulate in environments, provides run times longer than 8 hours in the 1000 to 5000 mL/min flow range, Programmable LCD clock timer, quite, small and lightweight for easy attachment to a worker's belt where it won't interfere with worker activity (Zefon International Inc., 2003). Air was drawn through a filter paper with support pad at an average flow rate of 3 L/min. Flow rate of air was verified by calibration both pre- and post-sample collection. The sampling pump used provides a non-fluctuating airflow through the filter and maintains the initial flow rate within $\pm 10\%$ throughout the sampling period.



Figure 3.2 GilAir-5 constant flow air sampling pump used during this research project (from Sensidyne Inc., 2001).

3.2.2 Filter Cassette

Lead particulate samples were collected using a closed-face sampling device consisting of three-polystyrene cassettes: cassette inlet, cassette ring and cassette outlet. The composition of the filter cassette is presented in Figure 3.3.

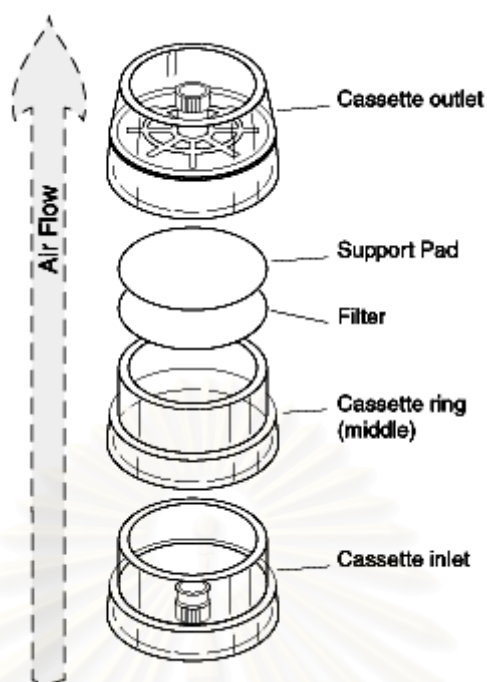


Figure 3.3 Filter cassette assembly used in this study (from SKC GULF COAST Inc., 2008)

All pieces of the cassette were cleaned using tap water followed by deionized water to eliminate any total suspended particulate matter before each cassette was plugged with plastic seals, shrink wrapped, labeled and kept in a clean plastic sealed bag.

3.2.3 Filter Paper

Mixed cellulose ester (MCE) membrane filters with pore sizes of $0.8\ \mu\text{m}$ and 37-mm diameter purchased from Advantec (CA-U.S.A.) were used in this investigation because they are suitable for air monitoring applications, dissolve completely using standard digestion procedures, offer minimal interference in fiber counting, possess low artifacts and meet NIOSH requirements for airborne metals monitoring (SKC Inc., 2008). The filter paper and support pad were stored in desiccators for at least 24 hour to remove any moisture content before use.

3.3 Sampling Sites

Chanthaburi is the most important center for gemstone processing and trading in Thailand; therefore, it was selected for the research area. However, only two factories were available for this study. This is due to the fact that heating techniques are secret processes of each factory. Thus even scientific research in gem treatment factories is hardly ever allowed. Besides, most of the gem treatment factories are also used as residences and family privacy is a concern. Nevertheless, both factories available for the study have different factors such as ventilator system and load of treated ruby that can be taken into correlation and interpretation. In addition, two residential home offices (i.e., internet café and restaurant) were selected as background sampling sites for correlation. The descriptions of all sampling sites are explained below:

3.3.1 Factory A

3.3.1.1 General Background

Factory A is a three and a half storey building. The first floor includes a living and dining room. The mezzanine has only a hall while the second floor has a bedroom. The third floor consists of a ruby heat-treatment room and a bedroom. Figure 3.4 shows the ruby heat-treatment room and the detail within this room. There are two electric furnaces which are used (Figure 3.5). The ventilation system of this room includes large vent holes, two opened slatted windows and a ventilator as shown in Figure 3.6.

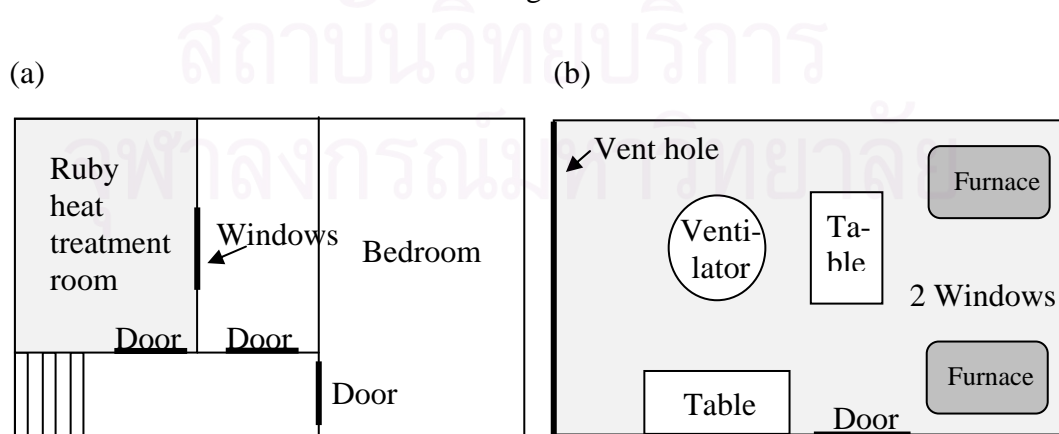
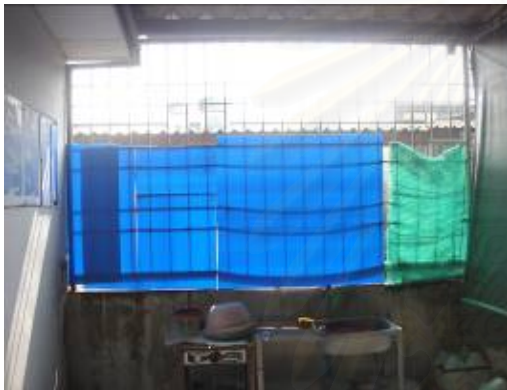


Figure 3.4 (a) Top view plan of the third floor in Factory A and (b) partitioning within the ruby heat treatment room.



Figure 3.5 Electric furnaces in the ruby heat-treatment room of Factory A.

(a)



(b)



Figure 3.6 (a) Vent holes and (b) 2-slatted window and a ventilator in Factory A.

3.3.3.2 Sampling Sites

1. Emission profile air samplers were placed on the gate of the furnace as shown in Figure 3.7 in order to study emission profile of lead particulate.



Figure 3.7 Sampling site at Factory A located above the gate of electric furnace.

2. Breathing zone, this zone was used to determine lead particulate concentration exposure of the treater during the ruby treatment procedure (mixing step and opening periods). We also monitored the time the treater was present at the home factory.

3. Indoor air air samplers were located near the table in the dining room on the first floor and in front of the treater's bedroom on the third floor as shown in Figures 3.8. This sampling plan was designed to determine lead concentration in indoor dust in different areas of the factory.

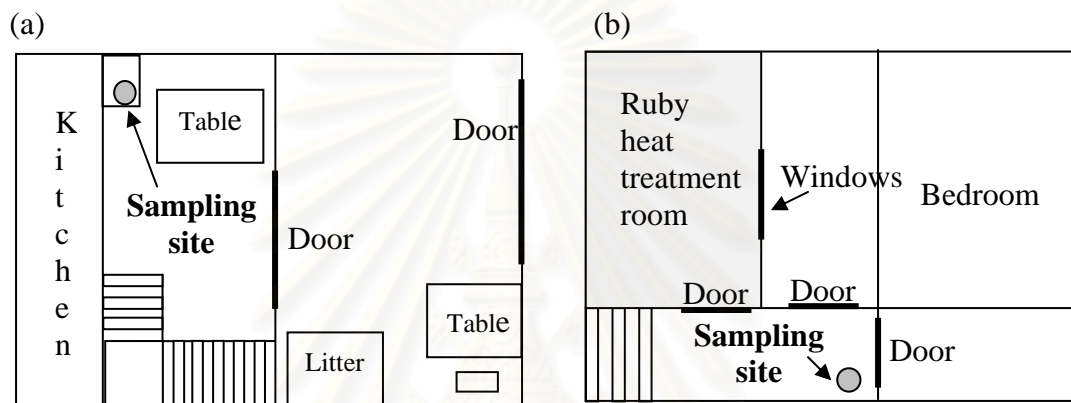


Figure 3.8 Indoor sampling sites in Factory A: (a) beside a table in dining room on the first floor and (b) in front of the treater's bedroom on the third floor.

3.3.2 Factory B

3.3.2.1 General Background

Factory B is a three and a half storey building. The first floor consists of living, dining and working areas. The second floor has a hall and small bedroom whereas the third floor contains only a bedroom. The areas used to conduct ruby treatment are a partial area on the first floor and the mezzanine between the first and second floors as shown in Figure 3.9.

Small vent holes in the walls on the first floor close to the doors are the major means of ventilation here. Although there is no window, two doors are situated in front and back sides of this floor (Figure 3.10). However, only the back door is opened during processing. On the mezzanine, there are three windows but they have never been opened (Figure 3.11). One wall has air vents. There are four

electric furnaces but only two of them are still operated. One furnace is used on the first floor and the other one is on the mezzanine as shown in Figures 3.12.

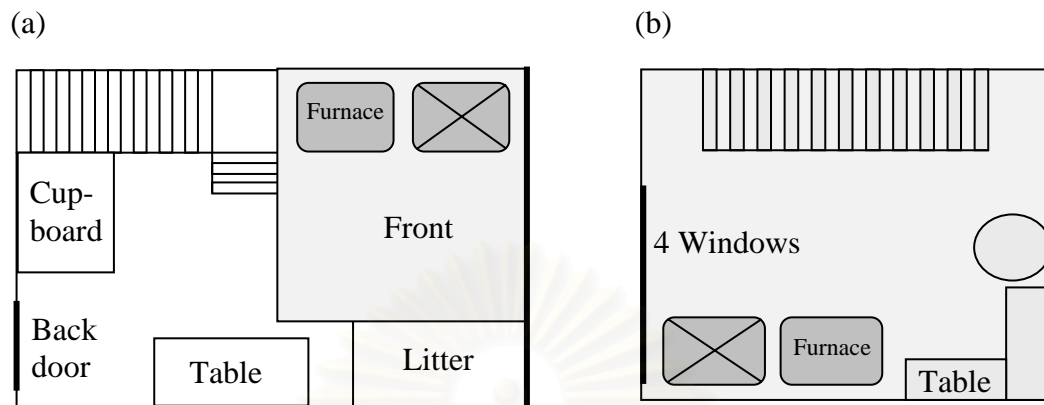


Figure 3.9 (a) Top view plan of the first floor and (b) mezzanine engaged for ruby heat-treatment in Factory B.

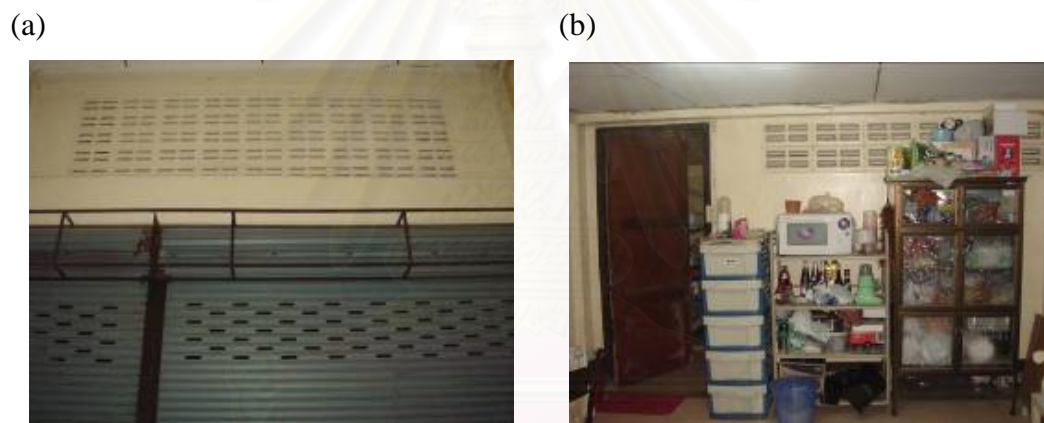


Figure 3.10 (a) Small vent holes above the front door and (b) back door downstairs on the first floor.



Figure 3.11 (a) Three windows always closed and (b) wall vent holes on the mezzanine.

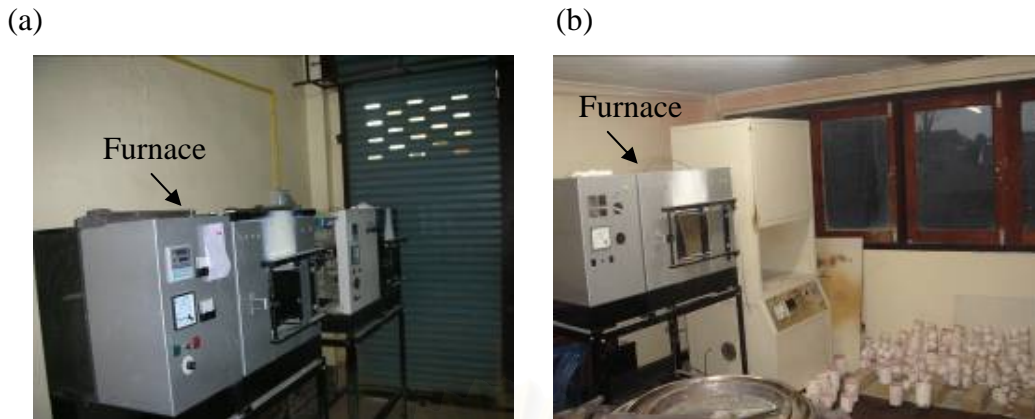


Figure 3.12 Electric furnaces used (a) on the first floor and (b) on mezzanine.

3.3.2.2 Sampling Sites

1. Air sampler was placed above the gate of the furnaces as shown in Figure 3.7. This study step is set to examine the lead particulate emission profile.

2. Breathing zone of the treater. This zone was used to determine lead concentration in particulate breathed by the treater during mixing step and gate opening period of ruby treatment process. In addition, monitoring time when the treater stayed at this home factory was also taken into account.

3. For indoor air examination, air sampler was designed to place on a table in living area on the first floor and in front of the treater's bedroom on the third floor as shown in Figures 3.13.

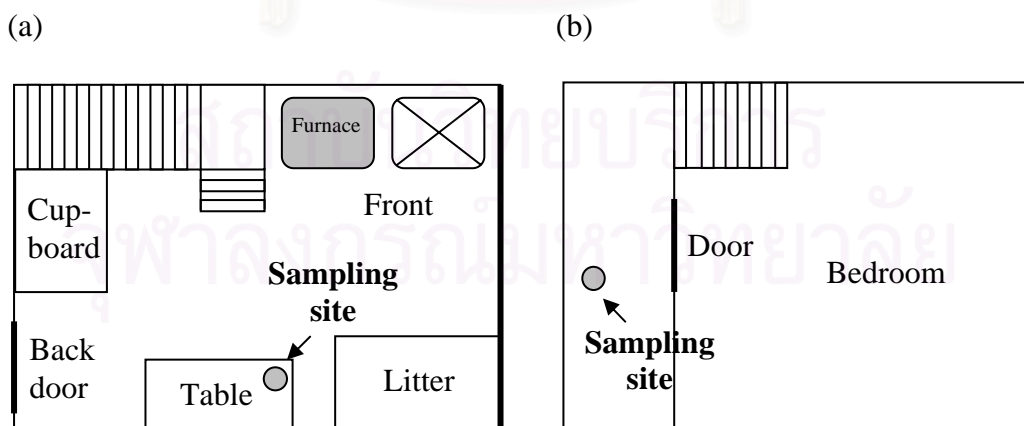


Figure 3.13 Sampling sites for indoor dust (a) on the first floor and (b) on the third floor.

3.3.3 Internet Café

Internet café is located in the center of Chanthaburi town about 1 km away from the gems market. It has two storeys; the second floor is used for residential area while the first floor is divided into two areas including internet café and dining area. Internet café is a closed air-conditioned room separated from dining room. Window and vent holes on the wall are the main ventilation system for the dining area. Personal sampling pump was placed on the table in the dining area in Figure 3.14(b) and air samples were drawn through the filter cassette with an average flow rate of 3 L/min.

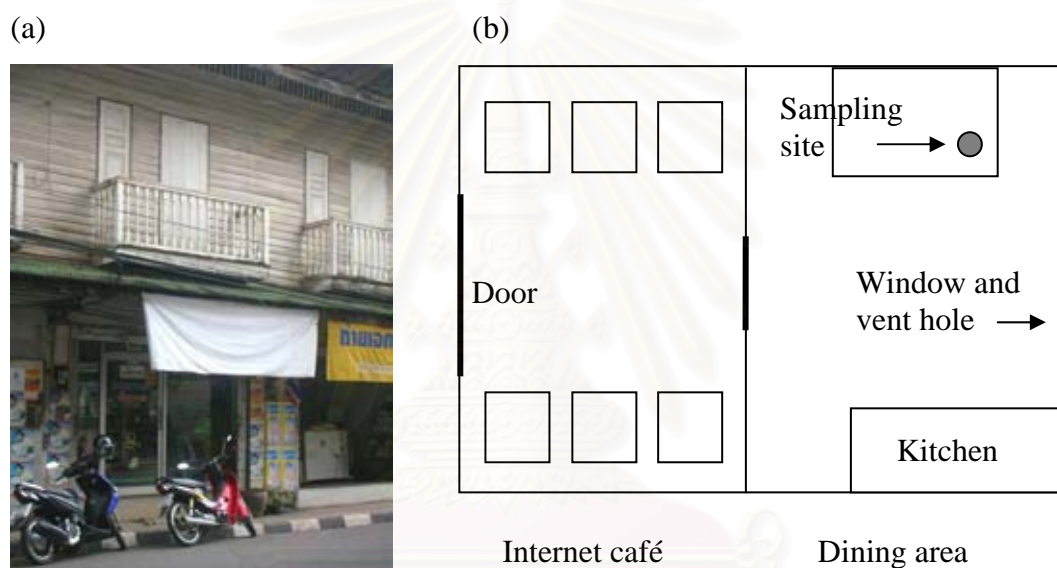


Figure 3.14 (a) Internet café taken as background location and (b) its top view plan of the first floor showing sampling site in the dining area.

3.3.4 Restaurant

Restaurant is located on the opposite side of road from the internet café. Three sliding doors situated at different locations are the main ventilation in this sampling site. There are three floors at this building of which only the first floor is used as a restaurant. Sampling collector was placed on a table on the first floor and flow rate of air was also adjusted at 3 L/min.

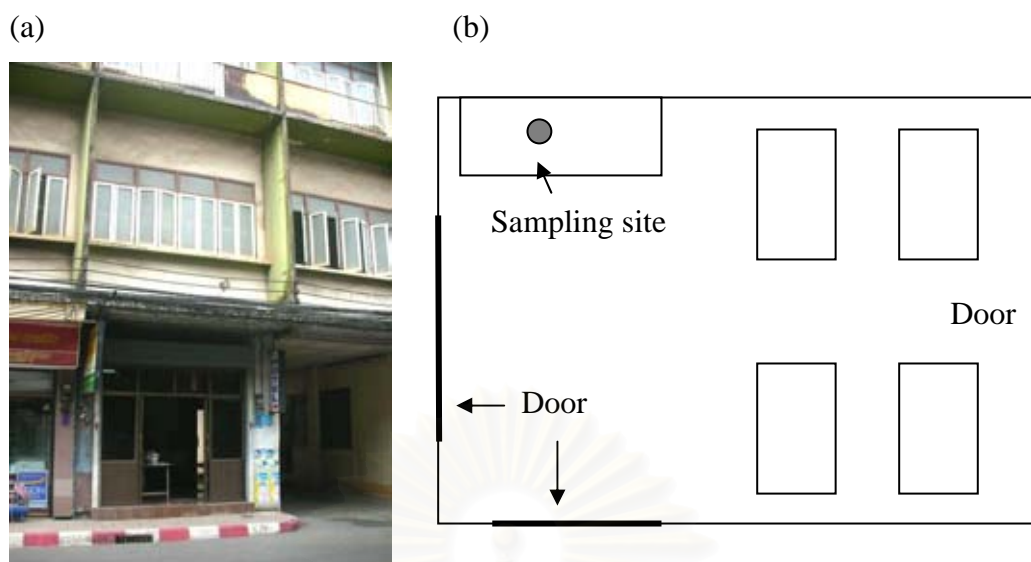


Figure 3.15 (a) Restaurant used as another background location and (b) its top view plan of the first floor showing sampling site in the restaurant.

3.4 Digestion Method

Hydrogen peroxide 30% and Nitric acid 65% analytical grade obtained from Merck (Darmstadt-Germany) were used for digestion as suggested by The National Institute for Occupational Safety and Health (NIOSH), lead by flame AAS 7082. The digestion method can be done following these steps:

1. Open the cassette filter holders and transfer the samples and blanks to clean beakers.
2. Add 3 mL conc. HNO_3 , and 1 mL 30% H_2O_2 and cover with a watch glass. Start reagent blanks at this step.
3. Heat on 140°C hotplates until volume is reduced to 0.5 mL.
4. Repeat two more times using 2 mL conc. HNO_3 and 1 mL 30% H_2O_2 each time and heat on 140°C hotplate until ca. 0.5 mL liquid remains.
5. When sample is dry, rinse the watch glass and walls of the beaker with 3 to 5 mL 10% HNO_3 . Allow the solution to evaporate to dryness.
6. Cool each beaker and dissolve the residues in 1 mL conc. HNO_3 .
7. Transfer the solution quantitatively to a 10-mL volumetric flask and dilute to volume with distilled water.
8. The solutions were analyzed for metal content by Atomic Absorption Spectrometer (Perkin Elmer, AAnalyst 800).

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Emission Profile of Lead Particulate from the Furnace

4.1.1 Each Step of Lead-Glass Heat Treatment Process

To study lead particulate emission profile from the ruby treatment furnace, lead particulate was collected above the gate of the electric furnace during heat-up, soaking and cooling step of heat treatment process of Factory B as reported in the last chapter. There were two sampling times in each treatment step including A and A* in heating up period, B and B* in soaking period, and C and C* in cooling down step, respectively (Figure 4.1). B* and C* sampling times were designed to cover short gate opening period between soaking and cooling step. In addition, weight of ruby for each treatment was also recorded to observe the effect of ruby load to lead emission.

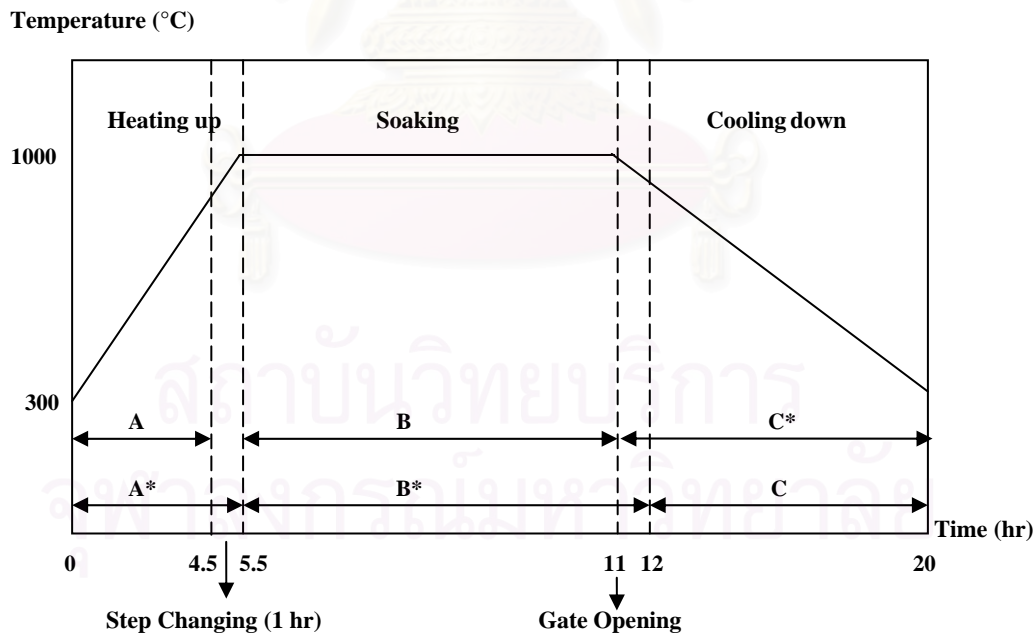


Figure 4.1 Sampling rounds in each step (heating up, soaking, and cooling down) of ruby heat treatment process.

The assumption of this sampling part is that lead particulate matter can emit from the furnace only during the gate opening period (between soaking

and cooling down steps); therefore, sampling plan can be divided into three rounds as described below.

(1) A and A* rounds

The aim of A and A* sampling rounds was to confirm that lead particulate cannot emit from the furnace when the gate was tightly closed. A and A* samples simultaneously started collecting in heating up period; however, the A round sampling was taken after 4.5 hours, about 1 hour before A*. Hence, if the assumption is right, lead concentration detected between A and A* rounds will not be different.

(2) B and B* rounds

B and B* samples were collected during soaking step. The lead particulate samples were collected at 6.5 hours for B* round from the soaking step (5.5 hours) plus one hour after the gate opening period while B was sampled only in soaking step (about 5.5 hours). It should be noted that the furnace gate is actually opened for just shot period (shorter than 10 min) to take the treated ruby out then it is promptly closed and left to cool down. Therefore, if the assumption is right, the difference of lead particulate concentration between B and B* sampling rounds will be detected.

(3) C and C* rounds

To confirm that lead particulate can emit during the gate opening period, the samples were collected in C* round by collecting promptly at the gate opening and continuously collected at hourly intervals of further cooling down for 8 hours. C round was started after the gate had been opened and closed for an hour then continuously collected during 8 hours of cooling down step.

Particulate collection was repeated 5 times for all sampling rounds under the same conditions at Factory B. Ruby weight, flow rate of air and sampling time were recorded to determine lead concentration in particulate emitted from the furnace at different periods of time during the whole treatment process. The results received from this step are summarized in Table 4.1.

Table 4.1 Lead particulate concentration (mg/m^3) from heat treatment process at different sampling periods.

| Weight of ruby (kg) | Lead concentration (mg/m^3) | | | | | |
|---------------------|---|-------|-------|-------|-------|-------|
| | A | A* | B | B* | C* | C |
| 0.5 | 0.001 | 0.001 | 0.002 | 0.055 | 0.043 | 0.000 |
| 2.0 | 0.000 | 0.001 | 0.002 | 0.221 | 0.237 | 0.003 |
| 2.5 | 0.002 | 0.003 | 0.002 | 0.225 | 0.271 | 0.003 |
| 3.0 | 0.001 | 0.003 | 0.006 | 0.283 | 0.359 | 0.003 |
| 4.5 | 0.004 | 0.004 | 0.009 | 0.413 | 0.379 | 0.005 |

In addition, plots of the results from Table 4.1 are illustrated in Figure 4.2. Where x axis is sampling rounds of heating up, soaking, and cooling down steps of ruby heat treatment process as described above and y axis is lead particulate concentration (mg/m^3).

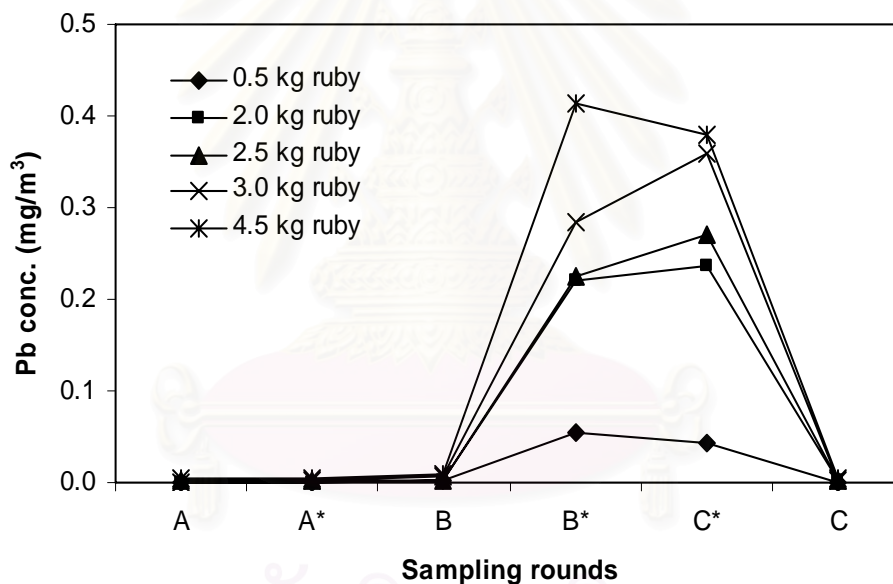


Figure 4.2 Lead particulate concentrations (mg/m^3) from heat treatment process.

Data illustrated in Table 4.1 and Figure 4.2 show that lead concentrations are not significantly different between A and A* rounds. This indicates that lead particulates could not emit from the furnace in heating up step because the gate of furnace was closed. However, if the weight of treated ruby exceeded 4 kg, lead concentration detected in both A and A* rounds slightly increased. This shows that even if the gate was tightly closed a small amount of lead can release from the furnace. When 0.5 kg of ruby was heat treated, 0.001 mg/m^3 of lead were detected in both A and A* rounds. The highest concentration

of lead (0.004 mg/m^3) found in both rounds was recorded from the treatment of the heaviest weight (4.5 kg) of ruby.

In B round, collected during soaking step before opening of furnace gate, lead concentrations are not different from those detected in A and A* rounds. On the other hand, samples collected in B* round, covering soaking step and furnace gate opening, yielded significantly much higher lead concentrations than those of former sampling periods; besides, concentrations of emitted lead particulate during this sampling round tended to be related to ruby load. The highest lead concentration (0.413 mg/m^3) appeared when the heaviest weight (4.5 kg) of ruby was heat treated.

Similar results also occurred in C* and C samplings. The concentrations of lead in C* round were higher than C. These concentrations also appear to depend upon the weight of treated ruby. 0.043 mg/m^3 was the lowest emitted lead concentration and was taken when the lowest load of ruby (0.5 kg) was heat treated while 0.379 mg/m^3 , the highest lead concentration emission was found when the highest weight of ruby (4.5 kg) was treated. In C round, the lead concentrations decreased greatly; the highest concentration equaled 0.005 mg/m^3 when 4.5 kg of ruby was treated.

In conclusion, lead is clearly emitted from the furnace at significant levels due to gate opening which is indicated by the results learned from this study step. In addition, lead concentration emitted directly from the furnace during an hour after the gate opening period can also be estimated as following. Amount of lead detected in B* round is subtracted by that detected in B round then the result is divided by the air volume subtraction between B* and B rounds. Results of this estimation are presented in Table 4.2. The same estimation is also applied for C* and C round; lead emission during an hour after gate opening yielded from this procedure is shown in Table 4.3. In comparison, lead emissions during an hour after gate opening estimated from B-B* rounds and C-C* round are quite close to each other.

Table 4.2 Estimation of lead concentration emitted during an hour after opening period using results from B* and B sampling rounds.

| Weight of ruby (kg) | Lead mass (mg) | | | Volume of air (m ³) | | | Lead conc. in particulate (mg/m ³) |
|---------------------|----------------|-------|-------|---------------------------------|-------|-------|--|
| | B* | B | B*-B | B* | B | B*-B | |
| 0.5 | 0.064 | 0.002 | 0.062 | 1.167 | 0.984 | 0.183 | 0.340 |
| 2.0 | 0.261 | 0.002 | 0.259 | 1.181 | 0.973 | 0.208 | 1.245 |
| 2.5 | 0.258 | 0.002 | 0.256 | 1.148 | 0.975 | 0.173 | 1.482 |
| 3.0 | 0.338 | 0.006 | 0.332 | 1.195 | 1.036 | 0.159 | 2.088 |
| 4.5 | 0.491 | 0.009 | 0.482 | 1.190 | 1.021 | 0.169 | 2.854 |

Table 4.3 Estimation of lead concentration emitted during an hour after opening period using results from C and C* sampling rounds.

| Weight of ruby (kg) | Lead mass (mg) | | | Volume of air (m ³) | | | Lead conc. in particulate (mg/m ³) |
|---------------------|----------------|-------|-------|---------------------------------|-------|-------|--|
| | C* | C | C*-C | C* | C | C*-C | |
| 0.5 | 0.070 | 0.001 | 0.069 | 1.625 | 1.408 | 0.217 | 0.319 |
| 2.0 | 0.365 | 0.004 | 0.361 | 1.541 | 1.275 | 0.266 | 1.359 |
| 2.5 | 0.423 | 0.004 | 0.419 | 1.562 | 1.303 | 0.259 | 1.619 |
| 3.0 | 0.593 | 0.004 | 0.589 | 1.653 | 1.412 | 0.241 | 2.445 |
| 4.5 | 0.622 | 0.007 | 0.615 | 1.642 | 1.436 | 0.206 | 2.986 |

Averages of lead concentration emitted during an hour after gate opening were determined using data estimated above and presented in Table 4.4. These results confirmed that lead particulates can emit from the furnace due to gate opening and higher amounts of lead emission are released from heavier loads of treated ruby. For example, 0.5 kg of treated ruby emitted 0.330 ± 0.015 mg/m³ of lead while 4.5 kg of treated ruby yielded 2.920 ± 0.094 mg/m³ lead emission. Although the other steps of heating emit trace amounts of lead emissions, which were determined not significant, they also slightly increase emission levels for treatments of higher ruby load.

Table 4.4 Average estimated lead concentration (mg/m^3) during an hour after gate opening.

| Weight of ruby (kg) | Estimated lead conc. in particulate (mg/m^3) | | |
|------------------------|--|-------|-------------------|
| | B*-B | C*-C | Average |
| 0.5 | 0.340 | 0.319 | 0.330 ± 0.015 |
| 2.0 | 1.246 | 1.359 | 1.302 ± 0.080 |
| 2.5 | 1.482 | 1.619 | 1.551 ± 0.097 |
| 3.0 | 2.088 | 2.445 | 2.266 ± 0.252 |
| 4.5 | 2.854 | 2.986 | 2.920 ± 0.094 |

4.1.2 Gate Opening Period

From the results in the previous section, we can conclude that lead particulate matter emits from the electric furnace in a significant amount when the gate opens and for an hour after the gate opening. For a clearer understanding of the emission path, lead particulate sampling was subdivided into 6 shorter rounds of 10 min sampling times. Figure 4.3 presents these 6 sampling rounds taken during the hour after gate opening. A personal sampling pump was placed above the gate of furnaces in the two ruby treatment factories (Factories A and B). Environment of both factories was reported in the last chapter.

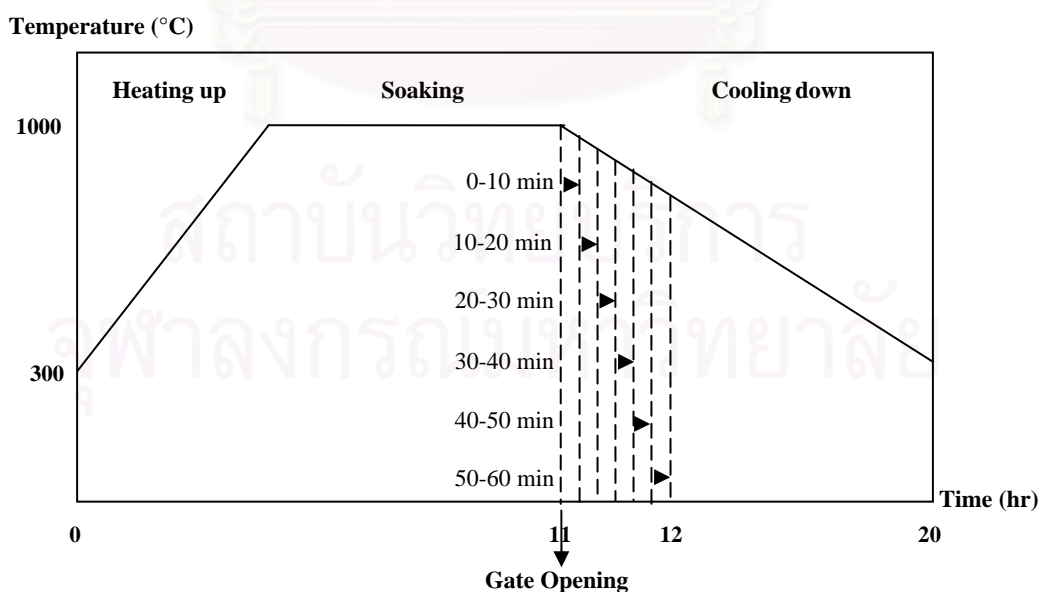


Figure 4.3 Six sampling rounds for ten minutes each during an hour after gate opening.

Two electric furnaces at Factory A and also two furnaces at Factory B were used in this study step. Sample collections were performed 5 times for every furnace. However, amounts of ruby and lead additive were not equal during each time of treatment. Analytical results obtained from the investigation are reported below.

4.1.2.1 Factory A

It should be noted that this factory is still experimenting with their ruby treatment; therefore, the ratio of lead-glass and ruby weight changed as they experimented to find the most suitable ratio. Consequently, amount of ruby and lead-glass additive used in each treatment was disclosed and recorded. Two electric furnaces (A-1 and A-2) are operated in this factory. Lead particulate emission profiles from both furnaces were examined with the following results.

(1) Furnace A-1

The results of lead particulate concentrations emission during an hour after gate opening obtained from Furnace A-1 are presented in Table 4.5. In 5 samplings, there was one trial of 25 g lead additive with 1.2 kg ruby and 76 g lead additive with 2.5 kg ruby for four trials.

Table 4.5 Lead concentration (mg/m^3) in particulate matter emitted in each ten minutes during an hour after gate opening from Furnace A-1.

| Weight of ruby (kg) | Weight of lead additive (g) | Lead concentration (mg/m^3) | | | | | |
|---------------------|-----------------------------|---|-----------|-----------|-----------|-----------|-----------|
| | | 0-10 min | 10-20 min | 20-30 min | 30-40 min | 40-50 min | 50-60 min |
| 1.2 | 25 | 0.576 | 0.022 | 0.019 | 0.007 | 0.004 | 0.003 |
| 2.5 | 76 | 3.502 | 0.043 | 0.035 | 0.025 | 0.014 | 0.013 |
| 2.5 | 76 | 2.972 | 0.090 | 0.081 | 0.047 | 0.028 | 0.016 |
| 2.5 | 76 | 3.090 | 0.076 | 0.087 | 0.024 | 0.043 | 0.038 |
| 2.5 | 76 | 4.215 | 0.121 | 0.072 | 0.083 | 0.054 | 0.018 |

Plots of the results reported in Table 4.5 are shown in Figure 4.4. Where x axis is sampling rounds during an hour after gate opening and y axis is lead concentration (mg/m^3) in particulate matter.

These results clearly demonstrate that lead particulate emission from the furnace at the first 10 min yields the highest concentrations of all times of treatment and it decreases rapidly after that. Most trials yield less than 0.1 mg/m³ and tend to decrease slightly during further sampling. In addition, higher weights of lead additive and ruby also give higher lead concentration emitted from the furnace.

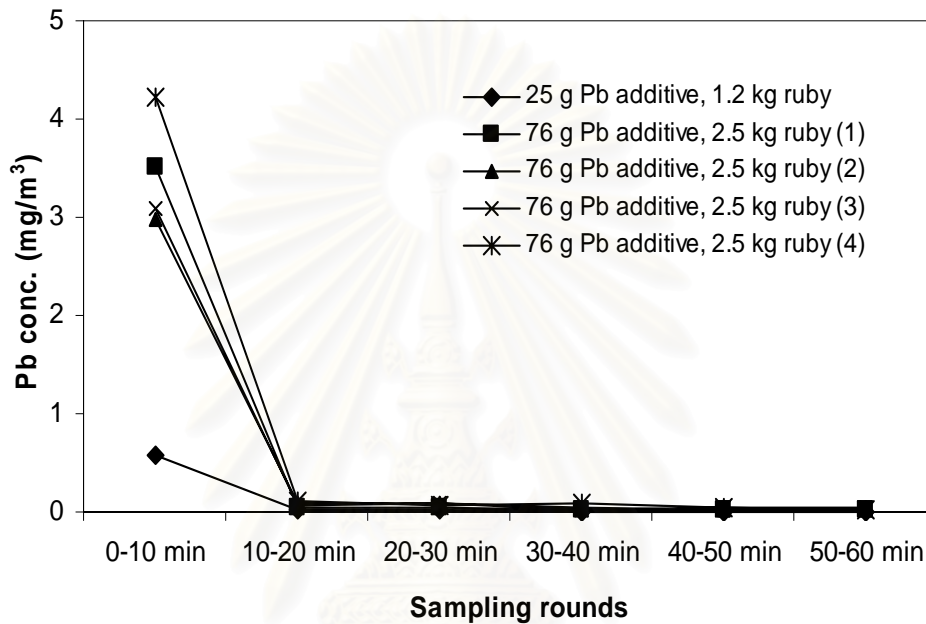


Figure 4.4 Lead concentrations (mg/m³) emitted during an hour after gate opening period from Furnace A-1.

As the results indicate, 25 g lead additive with 1.2 kg ruby emitted 0.576 mg/m³ of lead particulate within the first 10 min and emitted lead concentration decreased to 0.022 mg/m³ within the next 10 min. Subsequently, it continuously decreased to 0.003 mg/m³ within the last 10 min of sampling. On the other hand, 76 g lead additive with 2.5 kg ruby yielded higher lead concentrations during the whole cycle; averages of lead concentration were calculated for comparison. Lead concentration of about 3.445±0.562 mg/m³ were obtained within the first 10 min and it rapidly decreased to about 0.083±0.032 mg/m³ within the next 10 min; subsequently, lead concentration gradually declined to 0.021±0.011 mg/m³ in the last 10 min.

(2) Furnace A-2

Table 4.6 and Figure 4.5 present lead concentration emitted during an hour after gate opening of Furnace A-2. The 5 times of sampling, included onetime each of 20 g lead additive with 1.0 kg ruby and 25 g lead additive with 1.2 kg ruby and three times of 50 g lead additive with 2.0 kg ruby.

Table 4.6 Lead concentration (mg/m^3) in particulate matter emitted in each ten minutes during an hour after gate opening from Furnace A-2.

| Weight of ruby (kg) | Weight of lead additive (g) | Lead concentration (mg/m^3) | | | | | |
|---------------------|-----------------------------|---|-----------|-----------|-----------|-----------|-----------|
| | | 0-10 min | 10-20 min | 20-30 min | 30-40 min | 40-50 min | 50-60 min |
| 1.0 | 20 | 0.252 | 0.020 | 0.001 | 0.002 | 0.001 | 0.000 |
| 1.2 | 25 | 0.432 | 0.014 | 0.006 | 0.002 | 0.001 | 0.003 |
| 2.0 | 50 | 3.102 | 0.108 | 0.076 | 0.025 | 0.014 | 0.011 |
| 2.0 | 50 | 2.733 | 0.075 | 0.074 | 0.034 | 0.025 | 0.008 |
| 2.0 | 50 | 2.450 | 0.086 | 0.093 | 0.041 | 0.017 | 0.003 |

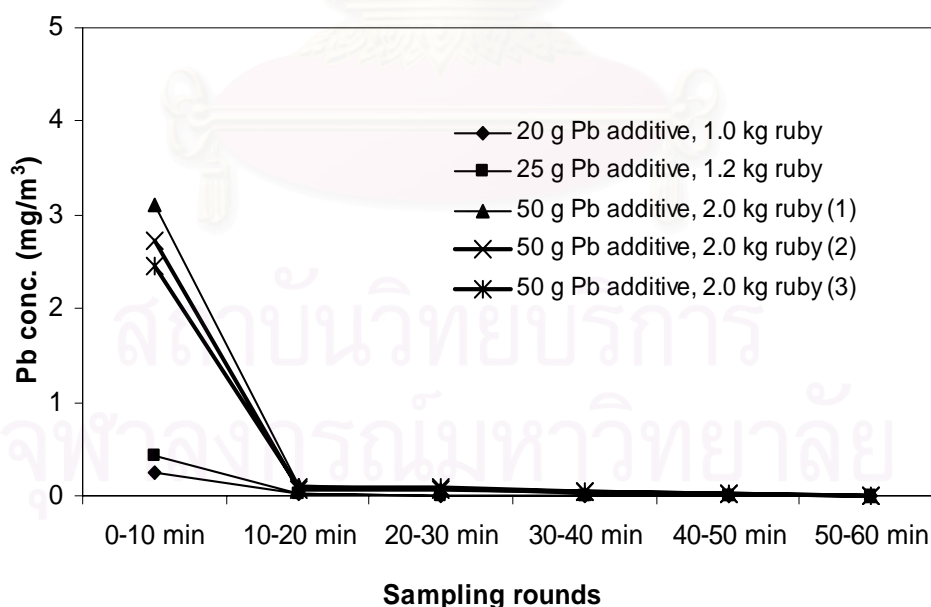


Figure 4.5 Lead concentrations (mg/m^3) emitted during an hour after gate opening period from Furnace A-2.

Similar to results that were obtained from Furnace A-1, the lead particulate emitted from furnace A-2 yielded the highest value within the first 10 min for all sampling sets. After that it decreased rapidly in the next 10 min and then declined gradually during further sampling. Moreover, the amount of lead additive was a significant factor effecting concentration of lead emission.

From Table 4.6 and Figure 4.5, 20 and 25 g of lead additive added in 1.0 and 1.2 kg of ruby for treatments caused the highest lead particulate concentration emission from the furnace within the first 10 min at 0.252 and 0.432 mg/m³ and then they decreased to 0.020 and 0.014 mg/m³ in next 10 min with continuously declining to 0.000 and 0.003 mg/m³ in the last 10 min, respectively. An average highest concentration of lead particulate emitted from treatment of 50 g lead additive with 2.0 kg ruby was equal to 2.762±0.327 mg/m³ then, in next 10 min it rapidly decreased to 0.090±0.017 mg/m³ and gradually continued decreasing during further sampling to 0.007±0.004 mg/m³ at the last 10 min.

4.1.2.2 Factory B

There are two furnaces in factory B: Furnace B-1 and B-2. Furnace B-1 is located on the first floor of the factory. It is usually used for medium to large size ruby heat treatment. Furnace B-2 is on the mezzanine and used to treat small-size ruby. This is because different sizes of ruby require different conditions for proper heat treatment. Small-size ruby must be treated by adding more amounts of lead additives and heated to a little higher soaking temperature than those applied for larger sized ruby. In this factory, the treater has never weighed lead additive before mixing with gems material; he mixes certain weights of ruby with an estimated quantity of lead additive and keeps the exact ingredients as a personal secret. Although weight of ruby can be recorded, exact quantity of lead additive could not be determined for each treatment performed in this factory.

(1) Furnace B-1

Lead concentrations emitted from Furnace B-1 within every 10 min of an hour after gate opening are presented in Table 4.7 and plotted in Figure 4.6. In 5 times of sampling, there were two times of treatment performed for 0.5 kg ruby and one time each for 2.0, 3.0, and 4.0 kg of ruby.

Table 4.7 Lead concentration (mg/m^3) in particulate matter emitted in each ten minutes during an hour after gate opening from Furnace B-1.

| Weight of ruby (kg) | Lead concentration (mg/m^3) | | | | | |
|---------------------|---|-----------|-----------|-----------|-----------|-----------|
| | 0-10 min | 10-20 min | 20-30 min | 30-40 min | 40-50 min | 50-60 min |
| 0.5 | 2.092 | 0.059 | 0.042 | 0.044 | 0.017 | 0.007 |
| 0.5 | 1.528 | 0.090 | 0.053 | 0.045 | 0.028 | 0.006 |
| 2.0 | 6.494 | 0.109 | 0.082 | 0.068 | 0.041 | 0.005 |
| 3.0 | 7.935 | 0.184 | 0.125 | 0.107 | 0.045 | 0.049 |
| 4.0 | 10.856 | 0.202 | 0.139 | 0.103 | 0.095 | 0.061 |

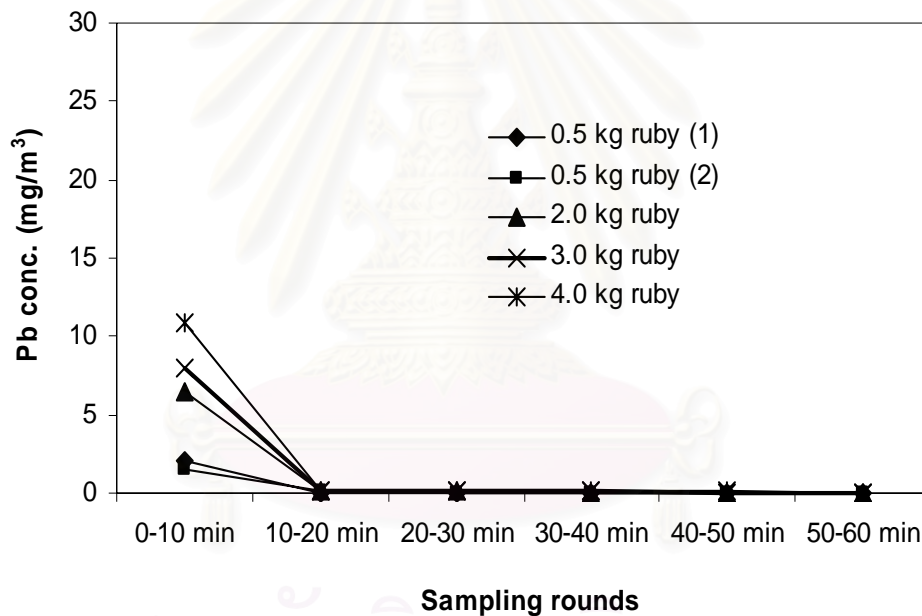


Figure 4.6 Lead concentrations (mg/m^3) emitted during an hour after gate opening period from Furnace B-1.

Lead emission profile of this furnace is also similar to those obtained from Furnaces A-1 and A-2 of Factory A. The highest concentration of lead was detected within the first 10 min of every sampling set and after that it decreased rapidly in the next 10 min and declined gradually during the further sampling rounds. In addition, Figure 4.6 also reveals clearly that the higher load of ruby emitted highest amount of lead particulate. At the first 10 min, treatment of 0.5 kg ruby emitted an average lead concentration of about $1.810 \pm 0.399 \text{ mg}/\text{m}^3$

whereas lead concentrations of 6.494, 7.935, and 10.856 mg/m³ were detected respectively from treatments of 2.0, 3.0, and 4.0 kg ruby. Subsequently, lead concentrations decreased rapidly in the next 10 min of sampling and declined gradually throughout the sampling time. In the last 10 min of sampling, an average lead particulate concentration emitted from 0.5 kg ruby treatment was equal to 0.007±0.001 mg/m³ and lead concentrations of 0.005, 0.049, and 0.061 mg/m³ were emitted from treatments of 2.0, 3.0, and 4.0 kg ruby, respectively.

(2) Furnace B-2

Table 4.8 and Figure 4.7 present lead concentrations emitted within each 10 min during an hour after gate of Furnace B-2 opened. The 5 samplings include onetime treatment for 2.0 and 3.5 kg ruby and three times of 5.0 kg ruby treatment.

Table 4.8 Lead concentration (mg/m³) in particulate matter emitted in each ten minutes during an hour after gate opening from Furnace B-2.

| Weight of ruby (kg) | Lead concentration (mg/m ³) | | | | | |
|---------------------|---|-----------|-----------|-----------|-----------|-----------|
| | 0-10 min | 10-20 min | 20-30 min | 30-40 min | 40-50 min | 50-60 min |
| 2.0 | 8.105 | 0.039 | 0.026 | 0.022 | 0.018 | 0.006 |
| 3.5 | 15.097 | 0.080 | 0.051 | 0.023 | 0.019 | 0.003 |
| 5.0 | 17.410 | 0.163 | 0.071 | 0.088 | 0.090 | 0.016 |
| 5.0 | 19.176 | 0.140 | 0.123 | 0.070 | 0.061 | 0.049 |
| 5.0 | 25.420 | 0.164 | 0.149 | 0.110 | 0.095 | 0.083 |

Figure 4.7 presents plots of lead particulate concentrations emitted from Furnace B-2 against sampling times during an hour after gate opening. The highest lead concentration emitted from 2.0 and 3.5 kg ruby treatments were obtained from the first 10 min of sampling and equaled 8.105 and 15.097 mg/m³, respectively. A higher average lead concentration of 20.669±4.208 mg/m³ was calculated from the first 10 min sampling of three treatments of 5.0 kg ruby. In the next 10 min sampling round, concentrations of lead decreased rapidly to 0.156±0.014 mg/m³ for averaged three times of 5 kg ruby treatment, and 0.039 and 0.08 mg/m³ of 2.0, and 3.5 kg ruby treatments, respectively. After that all five

sampling sets yielded lead concentrations which declined gradually during further sampling times.

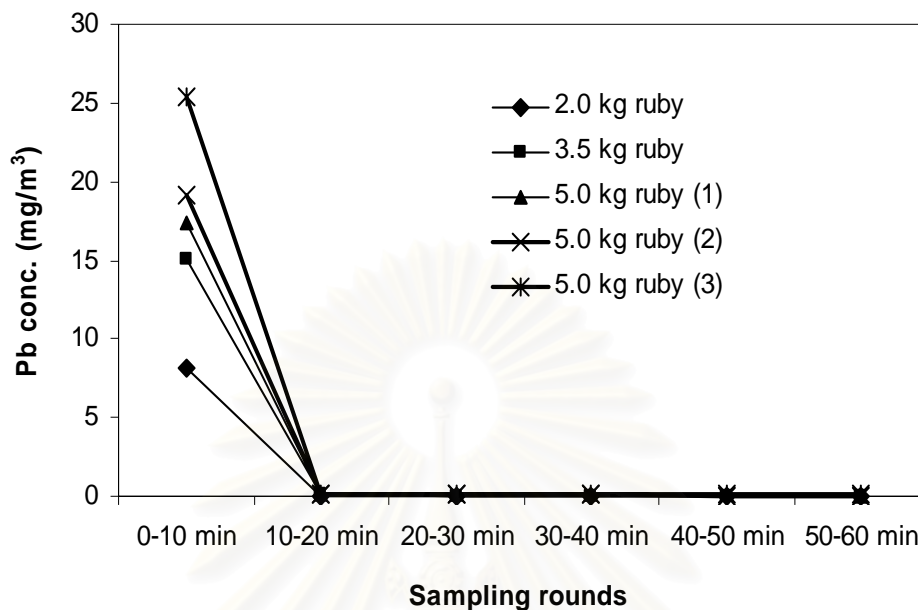


Figure 4.7 Lead concentrations (mg/m^3) emitted during an hour after gate opening period from Furnace B-2.

In conclusion, the results of lead particulate emission within each 10 min sampling during an hour after furnace gate opening from all furnaces (i.e., Furnaces A-1 and A-2 of Factory A and Furnaces B-1 and B-2 of Factory B) yielded similar trends. Lead-contaminated particulate is conclusively emitted from the furnace within the first 10 min after gate opening. In fact, treaters of both factories take a very short time (less than 10 min) to open the furnace gate and withdraw treated ruby; subsequently the gate is closed tightly. Hence, the lead concentrations detected after the first 10 min of gate opening may indicate roughly averaged concentration of lead particulates spreading around the furnace. In addition, higher amounts of lead additives used in the treatment result in higher lead emission throughout the sampling time. This holds not only within the first 10 min but also throughout the rest of an hour sampling sequence.

Moreover, amount of lead additive used in ruby treatment process directly effects concentration of lead emission from the furnace; therefore, the relationship between weight of lead additive (g) and emitted lead concentration (mg/m^3) obtained from Factory A can be used as a prediction of lead emission from the ruby treatment as follows:

4.1.3 Estimations of Lead Additive and Emission

4.1.3.1 Estimation of Lead Additive

Estimation of lead additive use is a very important environmental concern for the communities around the ruby treatment factories. These data may suggest environmental prevention to avoid the impact. Due to the fact that exact amount of the lead additive used in this industry is a personal secret, the concerned data cannot be collected directly from the general factory. Fortunately, some data collected from Factory A, which is still on an experimental process of ruby treatment, are available for this application. In order to estimate the amount of lead additive used in the process, the weight of lead additive (in gram) and lead concentration emission (mg/m^3) from monitoring within the first 10 min after gate opening are compared. The correlation is made on the fact that lead additive is highly exceeding for healing crack and fracture in rough ruby material, hence, the lead emission appears to be appropriately related to amount of lead additive. However, treatment of high weight ruby has to add more lead additive which such relation is also concerned and carried out in the next section.

Table 4.9 Weight of lead additive and emission concentration monitored at the first 10 min after gate opening from Furnaces A-1 and A-2.

| Furnace | Weight of lead additive (g), (x) | Lead concentration within first 10 min (mg/m^3), (y) |
|----------------|---|---|
| A-1 | 25 | 0.576 |
| | 76 | 3.502 |
| | 76 | 2.972 |
| | 76 | 3.090 |
| | 76 | 4.215 |
| A-2 | 20 | 0.252 |
| | 25 | 0.432 |
| | 50 | 3.102 |
| | 50 | 2.733 |
| | 50 | 2.450 |

The data available for the correlation between lead additive and lead emission are summarized in Table 4.9 and plotting of the results from furnaces A-1 and A-2 is presented in Figure 4.8. Where x axis represents lead particulate concentration (mg/m^3) emitted from the furnace at the first 10 min after gate opening period and y axis is weight of lead additive (g). Subsequently, linear equations of both plots are fitted.

The correlation between weight of lead additive and lead emission is presented in the form of linear equations below.

$$y = 15.544x + 21.172 \dots\dots\dots (4.1)$$

$$y = 11.067x + 19.148 \dots\dots\dots (4.2)$$

where y is weight of lead additive (g) and x is lead emission concentration (mg/m^3).

Equation 4.1 is the linear equation yielded from Furnace A-1 presenting R^2 of 0.874 whereas equation 4.2 is a linear equation resulted from Furnace A-2 giving R^2 of 0.966. Equation 4.1 has a somewhat low value of R^2 while equation 4.2 tends to have lower estimation of lead additive at high concentrations of lead emission. Therefore, plotting the results of Furnace A-1 and A-2 together was carried out and illustrated in Figure 4.9. A linear equation of raw data plotting is constructed and shown as equation (4.3) in Figure 4.9 (a) while Figure 4.9(b) shows a linear equation from plotting of averaged values (equation (4.4)). Linear equations from both plots are shown below and give R^2 values of 0.856 and 0.939, respectively. Slopes of both equations are close to each other; hence, the estimation of lead additive using equation (4.4) should yield more proper results.

$$y = 15.239x + 16.857 \dots\dots\dots (4.3)$$

$$y = 15.586x + 15.622 \dots\dots\dots (4.4)$$

where y is weight of lead additive (g) and x is lead emission concentration (mg/m^3).

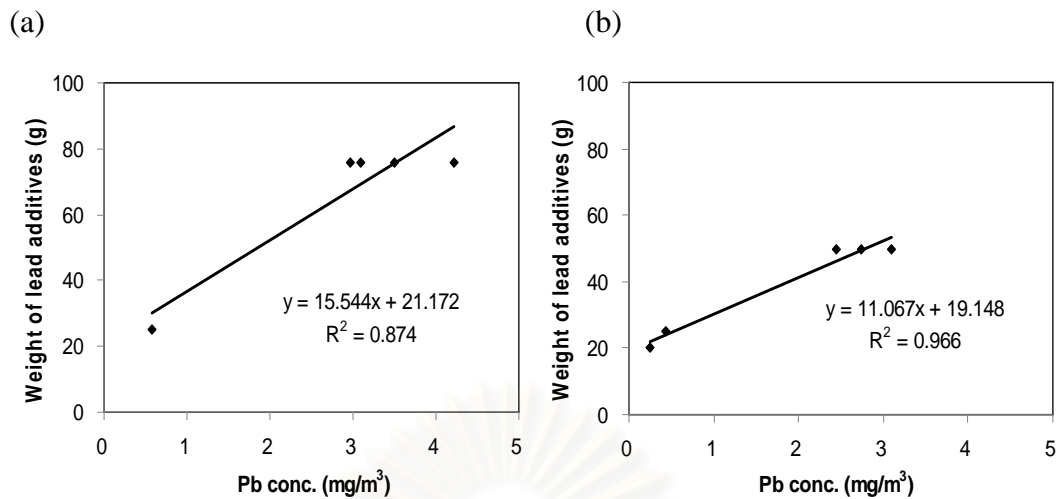


Figure 4.8 The relation between weight of lead additive and lead concentration emitted from the furnace including the fitting of linear equations of (a) Furnace A-1 and (b) Furnace A-2.

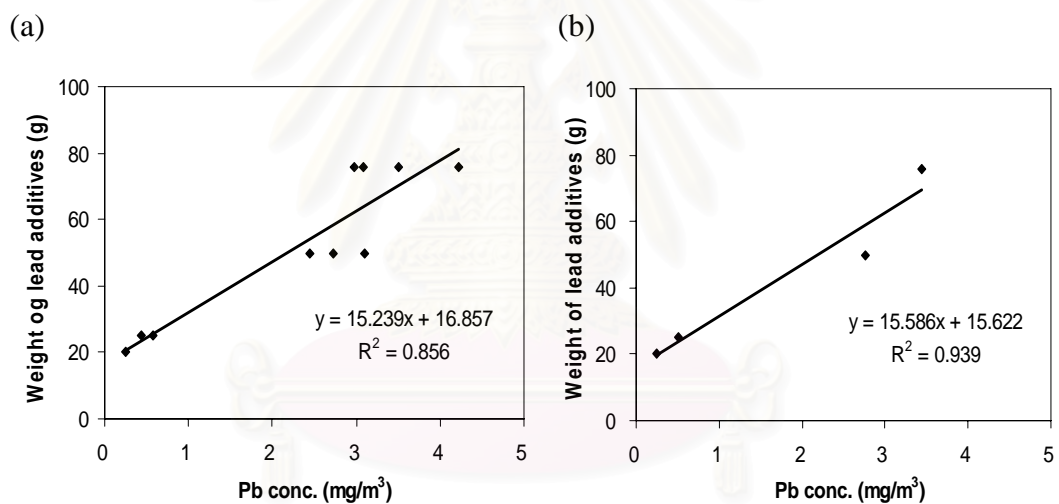


Figure 4.9 The relation between weight of lead additive and lead concentration emitted from the furnace including the fitting of linear equations of raw data (a) and averaged values (b) obtained from Furnaces A-1 and A-2.

All four linear equations can be used to estimate the amount of lead additives from monitoring data of lead emission from the furnace. However, equations 4.1 and 4.2 are constructed from individual data of Furnaces A-1 and A-2 which may not be suitable for wide-range estimation. On the other hand, the last two equations are constructed from combined data set of two furnaces; hence, these equations would be more suitable for empirical prediction of lead-glass

additives use. These additives are estimated from equations 4.1, 4.2, 4.3, and 4.4 as summarized in Table 4.10.

After comparing estimated lead additive and real records, equations 4.1, 4.2, 4.3, and 4.4 show errors of 18%, 12%, 13%, and 11% respectively. This indicates that Equation 4.4 is more suitably used to estimate weight of lead additive used in ruby treatment process than the other three equations.



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Table 4.10 Prediction of lead additive used in ruby treatment process compared with real record from Factory A.

| Furnace | Lead Conc. (mg/m ³), (x) | Lead additive used in the treatment (g), (y) | Equation 4.1 | | Equation 4.2 | | Equation 4.3 | | Equation 4.4 | |
|----------------|--------------------------------------|--|-----------------------------|-----------|-----------------------------|-----------|-----------------------------|-----------|-----------------------------|-----------|
| | | | Estimated lead additive (g) | % Error | Estimated lead additive (g) | % Error | Estimated lead additive (g) | % Error | Estimated lead additive (g) | % Error |
| A-1 | 0.576 | 25 | 30 | 20 | 26 | 4 | 26 | 4 | 25 | 0 |
| | 3.502 | 76 | 76 | 0 | 58 | 24 | 70 | 8 | 70 | 8 |
| | 2.972 | 76 | 67 | 12 | 52 | 32 | 62 | 18 | 62 | 18 |
| | 3.090 | 76 | 69 | 9 | 53 | 30 | 64 | 16 | 64 | 16 |
| | 4.215 | 76 | 87 | 14 | 66 | 13 | 81 | 7 | 81 | 7 |
| A-2 | 0.252 | 20 | 25 | 25 | 22 | 10 | 21 | 5 | 20 | 0 |
| | 0.432 | 25 | 28 | 12 | 24 | 4 | 23 | 8 | 22 | 12 |
| | 3.102 | 50 | 69 | 38 | 53 | 6 | 64 | 28 | 64 | 28 |
| | 2.733 | 50 | 64 | 28 | 49 | 2 | 59 | 18 | 58 | 16 |
| | 2.450 | 50 | 59 | 18 | 46 | 8 | 54 | 8 | 54 | 8 |
| Average | | | | 18 | | 12 | | 13 | | 11 |

4.1.3.2 Estimation of Lead Emission

Weight of lead additive used in ruby treatment process is usually undisclosed; however, ruby weight could be recorded from the factory. Hence, the idea of estimating lead emission from ruby loading in the treatment process was initiated. This relation is made on the assumption that lead emission is closely related to excess lead additive that is applied to heal cracks and fractures of ruby. The remaining amount of lead material, probably higher than 95% of the initial amount, is partially emitted into the air. Available data from both Factories A and B were used for constructing empirical equations. Table 4.11 shows weights of ruby and lead concentration emission data from Factories A and B.

Table 4.11 Weight of ruby (kg) and lead concentration (mg/m^3) emitted within the first 10 min after gate opening, data from Factories A and B.

| Factory | Weight of ruby (kg) | Lead conc. emission (g) |
|---------|---------------------|-------------------------|
| A | 1.0 | 0.252 |
| | 1.2 | 0.576 |
| | 1.2 | 0.432 |
| | 2.0 | 3.102 |
| | 2.0 | 2.733 |
| | 2.0 | 2.450 |
| | 2.5 | 3.502 |
| | 2.5 | 2.972 |
| | 2.5 | 3.090 |
| | 2.5 | 4.215 |
| B | 0.5 | 2.092 |
| | 0.5 | 1.528 |
| | 2.0 | 6.494 |
| | 2.0 | 8.105 |
| | 3.0 | 7.935 |
| | 3.5 | 15.097 |
| | 4.0 | 10.856 |
| | 5.0 | 17.410 |
| | 5.0 | 19.176 |
| | 5.0 | 25.420 |

Plotting of these data for individual factories is shown in Figure 4.10. Then correlations are made in the form of linear equations as shown in equations 4.5 and 4.6 as following.

$$y = 2.229x - 1.992 \dots \dots \dots (4.5)$$

$$y = 4.078x - 1.027 \dots \dots \dots (4.6)$$

where x is ruby weight (kg) and y is emitted lead concentration (mg/m^3).

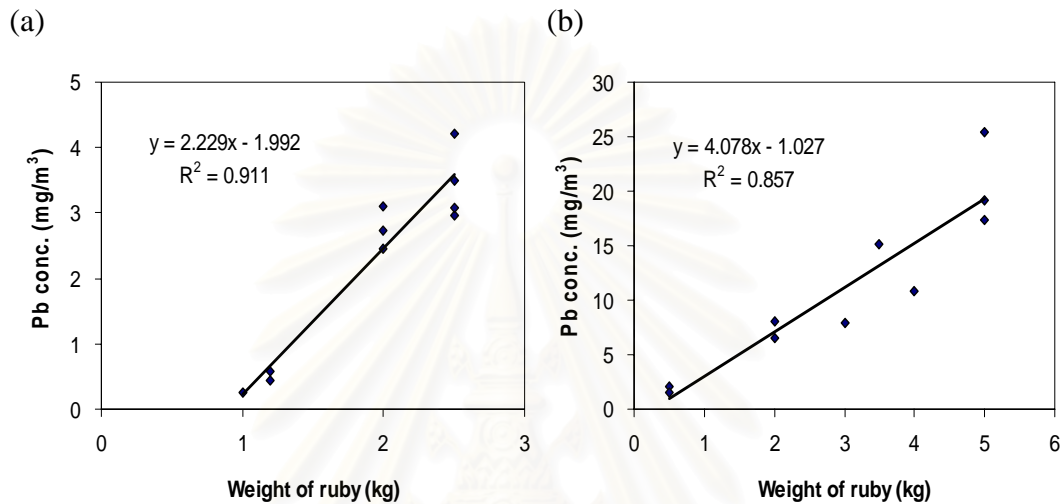


Figure 4.10 The relation between ruby weight and lead concentration emitted from the furnace including the fitting of linear equations of available data from Factory A (a) and Factory B (b).

In Factory A, the treater always weighs lead additive before mixing it with a given ruby weight; therefore, the ratio of lead additive and ruby weight is constant in all the treatments. Consequently, R^2 value (0.911) of equation 4.5 from Factory A is very high. On the other hand, the treater of Factory B has never weighed lead additive used in the process; thus, variation of lead additive versus treated ruby weight is wider than that of Factory A. Consequently, R^2 value of linear equation 4.6 is lower than that of equation 4.5; however, it is still acceptable value ($R^2 = 0.857$). Besides, slope of equation 4.6 is higher than slope of equation 4.5. This may be due to higher amounts of lead additive per kilogram of ruby being applied in Factory B and possibly yielding an over estimation of lead emission using this equation, particularly when small amounts of ruby are treated.

Subsequently, combined data set of both factories was plotted again and is shown in Figure 4.11. Reflecting the whole range of raw data to which averaged value of the same ruby load are separately applied.

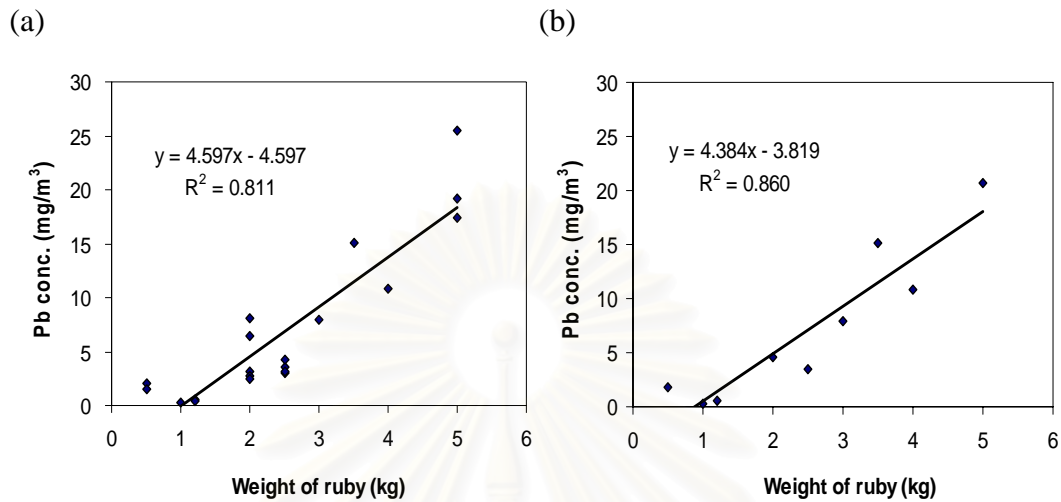


Figure 4.11 The relation between weight of ruby and lead concentration emitted from the furnace including the fitting of linear equations of raw data from both Factories A and B (a) and their average data (b).

Linear equations are consequently constructed from plots in Figure 4.11(a) and 4.11(b) as shown below.

$$y = 4.597x - 4.597 \dots \dots \dots (4.7)$$

$$y = 4.384x - 3.819 \dots \dots \dots (4.8)$$

where x is ruby weight (kg) and y is lead concentration emission (mg/m^3).

R^2 value of equation 4.7 is 0.811 a little lower than R^2 value (0.860) of equation 4.8. However, both equations are quite similar. Therefore, both equations are used to estimate lead emission within the first 10 min after gate opening. Table 4.12 shows results of estimation and % error of equations 4.5 to 4.8.

Table 4.12 Estimation of lead concentration emission within first 10 min after gate opening using equations 4.5 to 4.8.

| Factory | Weight of ruby (kg), (x) | Lead conc. measured from the treatment (mg/m ³), (y) | Equation 4.5 | | Equation 4.6 | | Equation 4.7 | | Equation 4.8 | |
|----------------|--------------------------|--|---|-----------|---|------------|---|-----------|---|-----------|
| | | | Estimated lead conc. (mg/m ³) | % Error | Estimated lead conc. (mg/m ³) | % Error | Estimated lead conc. (mg/m ³) | % Error | Estimated lead conc. (mg/m ³) | % Error |
| A | 1.0 | 0.252 | 0.237 | 6 | 3.051 | 1111 | 0.000 | 100 | 0.565 | 124 |
| | 1.2 | 0.432 | 0.683 | 58 | 3.867 | 795 | 0.919 | 113 | 1.442 | 234 |
| | 1.2 | 0.576 | 0.683 | 19 | 3.867 | 571 | 0.919 | 60 | 1.442 | 150 |
| | 2.0 | 3.102 | 2.466 | 21 | 7.129 | 130 | 4.597 | 48 | 4.949 | 60 |
| | 2.0 | 2.733 | 2.466 | 10 | 7.129 | 161 | 4.597 | 68 | 4.949 | 81 |
| | 2.0 | 2.450 | 2.466 | 1 | 7.129 | 191 | 4.597 | 88 | 4.949 | 102 |
| | 2.5 | 3.502 | 3.581 | 2 | 9.168 | 162 | 6.896 | 97 | 7.141 | 104 |
| | 2.5 | 2.972 | 3.581 | 20 | 9.168 | 208 | 6.896 | 132 | 7.141 | 140 |
| | 2.5 | 3.090 | 3.581 | 16 | 9.168 | 197 | 6.896 | 123 | 7.141 | 131 |
| | 2.5 | 4.215 | 3.581 | 15 | 9.168 | 118 | 6.896 | 64 | 7.141 | 69 |
| B | 0.5 | 2.092 | -0.878 | 142 | 1.012 | 52 | -2.299 | 210 | -1.627 | 178 |
| | 0.5 | 1.528 | -0.878 | 157 | 1.012 | 34 | -2.299 | 250 | -1.627 | 206 |
| | 2.0 | 6.494 | 2.466 | 62 | 7.129 | 10 | 4.597 | 29 | 4.949 | 24 |
| | 2.0 | 8.105 | 2.466 | 70 | 7.129 | 12 | 4.597 | 43 | 4.949 | 39 |
| | 3.0 | 7.935 | 4.695 | 41 | 11.207 | 41 | 9.194 | 16 | 9.333 | 18 |
| | 3.5 | 15.097 | 5.810 | 62 | 13.246 | 12 | 11.493 | 24 | 11.525 | 24 |
| | 4.0 | 10.856 | 6.924 | 36 | 15.285 | 41 | 13.791 | 27 | 13.717 | 26 |
| | 5.0 | 17.410 | 9.153 | 47 | 19.363 | 11 | 18.388 | 6 | 18.101 | 4 |
| | 5.0 | 19.176 | 9.153 | 52 | 19.363 | 1 | 18.388 | 4 | 18.101 | 6 |
| | 5.0 | 25.420 | 9.153 | 64 | 19.363 | 24 | 18.388 | 28 | 18.101 | 29 |
| Average | | | | 45 | | 194 | | 76 | | 87 |

From Table 4.12, equation 4.5 shows an average error of estimation that falls within the range of 45% whereas equation 4.6 appears to estimate with unacceptably wide average error range (194%). Concerning equations 4.7 and 4.8, they were derived from the data monitored from both factories; the average errors of estimation obtained from these two equations are equal to 76% and 87%, respectively. All estimated equations appear to have huge error for estimation at small amounts of treated ruby; particularly, ruby weight less than 1.0 kg seems to be unusable for estimation in all four equations.

Equations 4.7 and 4.8 were expected to give more suitable prediction of lead concentration emission. In fact, their average errors are much higher than equation 4.5. This indicates that equation 4.5 is, in fact, more suitably used for estimation. However, equations 4.5, 4.6, 4.7, and 4.8 can still estimate lead emission concentration at 3.0 to 5.0 kg of the ruby treatment where narrow ranges of estimation error of 36-64%, 1-41%, 4-28% and 4-29% were obtained, respectively.

4.2 Exposure of the Treater to Lead Particulate

The aim of this sampling part was to measure the ruby treater exposure to lead concentration. Collections of particulate samples within the breathing zone were taken in both factories using a personal air sampler; the filter cassette was clipped on the collar of the treater. The suitable flow rate of the air was adjusted to 3 L/min (as recommended by Liu et al., 1985).

In Factory A, sampling plan was divided into two main parts following the treater's main activities. The first part was measurements of lead concentration during ruby-lead additive mixing step and gate opening which are related to the highest risk periods of this occupation. The second part is concerned with residence in the home factory; hence, air samples were collected all day (24 hours). For daytime, the cassette was clipped in breathing zone of the treater and at nighttime the sampling pump was placed in front of the treater's bedroom to avoid disturbances caused by the pumping noise.

Sampling plan of Factory B was slightly different from Factory A. Due to the fact that there are no people staying in the home factory during daytime, these samples were collected throughout the time treater stayed at home

factory. However, personal exposure effected by ruby treatment process, particularly mixing step and gate opening period were carried out in the same pattern as Factory A.

Table 4.13 presents personal exposure of the treater to lead concentrations (mg/m^3) during whole day monitoring, mixing step, and gate opening step at Factory A and Table 4.14 shows Personal exposure of treater during the resident period, mixing step and gate opening period at Factory B, respectively.

Personal lead concentration during ruby treatment process from Factories A and B were compared with the Thai occupational health standard which was recommended by Notification of Interior Ministry on chemicals in the workplace in 1977. An average concentration of lead and its inorganic compound to which a worker is exposed throughout the working time should not be higher than $0.2 \text{ mg}/\text{m}^3$. Moreover, international organizations have suggested occupational health standards for lead in the workplace. Occupational Safety and Health Administration (OSHA) has set Permissible Exposure Limit (PEL) for lead at $0.05 \text{ mg}/\text{m}^3$ as similar to the American Conference of Governmental Industrial Hygienists (ACGIH) and National Institute for Occupational Safety and Health (NIOSH) have recommended Threshold Limit Value (TLV) of lead at $0.05 \text{ mg}/\text{m}^3$. Both PEL and TLV are considered based on time weight average of 8 hours of working time.

In Factory A, the treater usually performs the treatment processes (mixing step and opening period) within the ruby treatment room. Except for those times, he stays elsewhere in the home. Therefore lead concentrations during whole day monitoring of this factory should be compared with ambient air quality standard. In contrast, Factory B ruby treatment area is not separate from living area. Two ruby treatment furnaces are located on first floor and mezzanine. Hence, lead concentration during resident time of the treater should be compared with the occupational health standard. So, for clearer understanding whole day lead concentrations in Factory A and lead concentrations during resident time in Factory B are compared with both occupational health standard and ambient air quality standard. Since occupational health standards are detailed in previous paragraphs only ambient air quality standards are described in this part. Pollution Control Department (PCD), Ministry of Natural Resource and Environment,

Thailand has recommended lead concentration in ambient air should not exceed 0.0015 mg/m³ (an average concentration within a month) whereas U.S. Environmental Protection Agency (U.S.EPA) has set National Ambient Air Quality Standards (NAAQS) for lead at 0.0015 mg/m³ (quarterly average).

Table 4.13 Personal exposure of the treater to lead concentrations (mg/m³) during whole day monitoring, mixing step, and gate opening step at Factory A.

| Furnace | Ruby weight (kg)/Lead additive (g) | Treater's personal exposure of lead concentration (mg/m ³) | | |
|---------|--|---|--------------------|--------------------|
| | | Whole day monitoring (24-hr) | Treatment process | |
| | | | Mixing step | Opening period |
| A-1 | 1.2/25 | 0.0012 | 0.016 | 0.012 |
| | 2.5/76 | 0.0015 ^a | 0.173 ^b | 0.192 ^b |
| | 2.5/76 | 0.0035 ^a | 0.123 ^b | 0.148 ^b |
| | 2.5/76 | 0.0018 ^a | 0.137 ^b | 0.126 ^b |
| | 2.5/76 | 0.0025 ^a | 0.170 ^b | 0.157 ^b |
| A-2 | 1.0/20 | 0.0007 | 0.009 | 0.005 |
| | 1.2/25 | 0.0015 ^a | 0.021 | 0.018 |
| | 2.0/50 | 0.0015 ^a | 0.103 ^b | 0.086 ^b |
| | 2.0/50 | 0.0007 | 0.124 ^b | 0.118 ^b |
| | 2.0/50 | 0.0010 | 0.095 ^b | 0.121 ^b |

Note: Thai ambient air quality standard and NAAQS for lead = 0.0015 mg/m³

PEL and TLV for lead = 0.05 mg/m³

Thai occupational health standard for lead and its inorganic compound = 0.2 mg/m³

^a Over Thai ambient air quality standard and NAAQS

^b Over PEL and TLV for lead

^c Over Thai occupational health standard

Table 4.14 Personal exposure to lead (mg/m^3) for the treater during resident period, mixing step and gate opening step at Factory B.

| Furnace | Ruby weight (kg) | Lead concentration exposed to treater (mg/m^3) | | | |
|---------|------------------|--|---------------------|----------------------|----------------------|
| | | Monitoring in resident period | | Treatment process | |
| | | Monitoring period (hr) | Conc. | Mixing step | Opening period |
| B-1 | 0.5 | 16.0 | 0.0015 ^a | 0.014 | 0.066 ^b |
| | 0.5 | 14.5 | 0.0028 ^a | 0.042 | 0.101 ^b |
| | 2.0 | 14.0 | 0.0017 ^a | 0.101 ^b | 0.242 ^{b,c} |
| | 3.0 | 16.0 | 0.0019 ^a | 0.127 ^b | 0.357 ^{b,c} |
| | 4.0 | 12.0 | 0.0025 ^a | 0.150 ^b | 0.452 ^{b,c} |
| B-2 | 2.0 | 14.5 | 0.0013 | 0.099 ^b | 0.276 ^{b,c} |
| | 3.5 | 16.0 | 0.0014 | 0.100 ^b | 0.310 ^{b,c} |
| | 5.0 | 16.0 | 0.0023 ^a | 0.216 ^{b,c} | 0.464 ^{b,c} |
| | 5.0 | 15.0 | 0.0025 ^a | 0.225 ^{b,c} | 0.628 ^{b,c} |
| | 5.0 | 14.5 | 0.0014 | 0.203 ^{b,c} | 0.627 ^{b,c} |

Note: Thai ambient air quality standard and NAAQS for lead = $0.0015 \text{ mg}/\text{m}^3$

PEL and TLV for lead = $0.05 \text{ mg}/\text{m}^3$

Thai occupational health standard for lead and its inorganic compound = $0.2 \text{ mg}/\text{m}^3$

^a Over Thai ambient air quality standard and NAAQS

^b Over PEL and TLV for lead

^c Over Thai occupational health standard

4.2.1 Personal Lead exposure during monitoring period

In Factory A, personal lead exposure concentrations detected during 24 hours of whole day monitoring were in the range of $0.0007\text{-}0.0035 \text{ mg}/\text{m}^3$. When compared with ambient air quality standard, they almost exceed both Thai and NAAQS ($0.0015 \text{ mg}/\text{m}^3$) standard. During this sampling period, although the treater did not perform the treatment process, he still went in and out of the ruby treatment room. Additionally, higher weight of ruby was treated leading to longer time being spent in the treatment room. The comparison with occupational health standard for this whole day lead concentration was much lower than both PEL and TLV standard ($0.05 \text{ mg}/\text{m}^3$) and Thai standard ($0.2 \text{ mg}/\text{m}^3$).

On the other hand, Factory B lead concentrations detected during the resident period almost exceed both Thai and NAAQS ($0.0015 \text{ mg}/\text{m}^3$) ambient

air quality standard. This may be due to the fact that the treatment area and furnaces are not separated from the living area in this factory. On the other hand when compared with occupational health standard, lead concentrations detected in all times of sampling were not higher than Thai (0.2 mg/m^3), PEL and TLV (0.05 mg/m^3) standard.

4.2.2 Personal Lead Exposure during Ruby Treatment Process

Factory A, lead concentrations in mixing step and opening period of furnace gate were extremely higher than those found during the whole day monitoring; this evidence indicates that ruby treatment processes (both mixing and opening steps) are the main causes of the personal lead exposure to the treater. When compare with 0.05 mg/m^3 of PEL and TLV standards for lead, it is found that the treater has significantly taken lead during both mixing step and opening period more than the permission, particularly at higher than 25 g of lead additive added. However, they are still below Thai occupational health standard value (0.2 mg/m^3).

In Factory B, lead concentration during ruby treatment process (mixing step and opening period) was found to be close to those of Factory A. Ruby treatment activities are conclusively the main cause of the lead particulate exposure to the treater. In mixing step, higher than 2.0 kg ruby treatments cause lead levels to the treater to exceed 0.05 mg/m^3 of PEL and TLV standards. Personal lead concentrations are higher than the Thai occupational health standard (0.2 mg/m^3) when 5.0 kg of ruby were treated. On the other hand, during opening period, personal lead concentration exceeds PEL and TLV standards, during the treatments for medium to high load of ruby (e.g., 2.0 to 5 kg); this tends to increase personal lead concentration to exceed 0.2 mg/m^3 of the Thai occupational health standard. Therefore, medium loads of ruby treatment, from 2.0 kg upward, have more possibility to cause high lead personal exposure; the treater is recommended to wear Personal Protective Equipment (PPE) such as a filter mask with cartridges during the gate opening. This is to protect from lead airborne particulate getting into the respiratory system. However, long term health effects should also be a great concern and it is recommended that the treater should always wear the mask during working time even if less than 2.0 kg of ruby is

treated. In addition, an effective ventilation system can get rid of some lead from this home factory.

4.3 Indoor Lead Particulate in Home Factories

The objective of this section is to measure lead concentration dispersing in indoor air within ruby-treatment home factory (i.e., Factories A and B). Air samples were drawn through the MCE filter at an average flow rate of 3 L/min; sampling heights were in the range of 1-1.5 m above floor level to represent the breathing level of occupants. Lead particulate collections were repeated more than 5 times in both factories.

In Factory A, the ruby treatment furnaces have been set in the treatment room on the third floor where it is separated from the living area mainly located on the first and second floors. The living area downstairs and the hallway outside the bedroom on third floor of Factory A (Figure 3.8) were used for sampling sites in this part. The ventilation system of the ruby treatment room consists of two slatted windows, large vent holes and ventilator (see also chapter 3).

In Factory B, the working area is not obviously separated from living area. One furnace is located near the dining area on the first floor and the other furnace is set on the mezzanine. The dining area on the first floor and area in front of the treater bedroom on third floor (Figure 3.13) were engaged as sampling sites in this factory. Only small vent holes provide the main ventilation in this factory.

Moreover, indoor lead concentrations in other residential home offices (i.e., internet café and restaurant) were measured. They are used as the background lead level and to confirm lead concentration in both factories lead-glass heat treatment process. Lead concentrations in indoor air can be used to indicate an average concentration of lead exposed to those who do not perform the treatment process but live in the home factory. From the literature reviews, there is no standard set for lead contamination in indoor air. All data has been adjusted on the basis of sampling time to compare with the standards which are available as follows: 1) Comparison with the occupational health standards (Thai, PEL and TLV), the samplings were divided into 3 periods (8 hours per period) including

from 6.00pm to 2.00am (period 1), from 2.00am to 10.00am (period 2), and from 10.00am to 6.00pm (period 3). 2) Subsequently, whole day concentrations (see Appendix B) were calculated to compare with ambient air quality of Thai and international standards based on an average 24 hour sampling time.

4.3.1 Background Lead Concentration

Background lead concentrations taken from home businesses (i.e., internet café and restaurant) are presented in Table 4.15. Indoor lead concentrations in both internet café and restaurant are very low and they are mostly much lower than the PEL and TLV standards of lead (0.05 mg/m^3) and Thai occupational health standard (0.2 mg/m^3). The highest lead concentrations in the internet café of all three periods equal 0.0004 , 0.0006 , and 0.0003 mg/m^3 , respectively while lead concentration in the restaurant during all three sampling periods is almost negligible. Lead concentrations detected in internet café seem to be higher than restaurant because the computers are repaired within dining area of the internet café. In addition, the lead concentrations through the whole day measured in these two home businesses are much lower than the Thai ambient air quality standard (0.0015 mg/m^3) and NAAQS standard (0.0015 mg/m^3). These findings indicate that the two background home businesses, which have never conducted ruby heat treatment, have very low indoor lead concentration.

Table 4.15 Indoor lead particulate concentrations (mg/m^3) of background collected from internet café and restaurant.

| Sampling site | Sampling time | Indoor lead conc. (mg/m^3) | | | |
|---------------|----------------|--|------------------------------|------------------------------|----------------------|
| | | Period 1 (6.00pm-2.00am) | Period 2 (2.00am-10.00am) | Period 3 (10.00am-6.00pm) | Whole day (24 hr) |
| Internet | 1 | 0.0002 | 0.0003 | 0.0001 | 0.0002 |
| | 2 | 0.0004 | 0.0006 | 0.0002 | 0.0004 |
| | 3 | 0.0001 | 0.0001 | 0.0001 | 0.0001 |
| | 4 | 0.0001 | 0.0001 | 0.0001 | 0.0001 |
| | 5 | 0.0003 | 0.0004 | 0.0003 | 0.0003 |
| | Average | 0.0002 | 0.0003 | 0.0002 | 0.0002 |
| Restaurant | 1 | ND | ND | ND | ND |
| | 2 | ND | 0.0001 | ND | ND |
| | 3 | ND | 0.0001 | ND | ND |
| | 4 | 0.0001 | ND | 0.0001 | ND |
| | 5 | ND | ND | 0.0001 | ND |
| | Average | 0.0001 | 0.0001 | 0.0001 | 0.0000 |

Note: Detection limit = $0.0001 \text{ mg}/\text{m}^3$

ND = non detected

PEL and TLV standard of lead = $0.05 \text{ mg}/\text{m}^3$

Thai occupational health standard for lead and its inorganic compound = $0.2 \text{ mg}/\text{m}^3$

Ambient air quality both Thai and NAAQS standard = $0.0015 \text{ mg}/\text{m}^3$

4.3.2 Indoor Lead Concentration in Factories A and B

Table 4.16 presents indoor lead particulate concentrations (mg/m^3) collected from Factory A at three different sampling periods and also whole day concentration. The highest lead concentrations of each sampling period taken from the first floor were 0.0016 , 0.0027 and $0.0020 \text{ mg}/\text{m}^3$. Maximums of 0.0018 , 0.0025 and $0.0014 \text{ mg}/\text{m}^3$ were obtained from the third floor. Lead concentration in Factory A is significantly higher than that detected within two background home businesses; however, all indoor lead concentrations found in this factory are lower than the PEL and TLV standard of lead ($0.05 \text{ mg}/\text{m}^3$) and the Thai occupational health standard ($0.2 \text{ mg}/\text{m}^3$).

Lead particulates detected during three sampling periods were calculated as whole day average. The maximum lead concentration within the first floor equaled 0.0016 mg/m^3 and that is not very different from the third floor reading of 0.0018 mg/m^3 . Results show that whole day lead concentrations are found higher in Factory A than in the two background homes. This indicates that the ruby treatment involving lead-glass additives is the main cause of lead emission within the ruby treatment home factory.

Whole day lead concentrations are almost below both Thai ambient air quality standard and NAAQS (0.0015 mg/m^3), however, only at one time of sampling did it exceed these standards. Whole day lead concentration detected on 1st floor was equal to 0.0016 mg/m^3 while on 3rd floor equal 0.0018 mg/m^3 , respectively. These data indicate that this factory is safe for use as a residential area even if the treatment process is conducted there.



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Table 4.16 Indoor lead particulate concentrations (mg/m^3) in Factory A at three different sampling periods and whole day average.

| Factory | Sampling time | Indoor lead concentration (mg/m^3) | | | | | | | |
|---------|---------------|--|-----------------------|------------------------------|-----------------------|------------------------------|-----------------------|------------------------------|-----------------------|
| | | Period 1 (6.00pm–2.00am) | | Period 2 (2.00am–10.00am) | | Period 3 (10.00am-6.00pm) | | Whole day average (24 hr) | |
| | | 1 st floor | 3 rd floor | 1 st floor | 3 rd floor | 1 st floor | 3 rd floor | 1 st floor | 3 rd floor |
| A | 1 | ND | ND | ND | ND | ND | ND | ND | ND |
| | 2 | 0.0006 | 0.0017 | 0.0016 | 0.0012 | 0.0018 | 0.0014 | 0.0013 | 0.0014 |
| | 3 | 0.0012 | 0.0013 | 0.0027 | 0.0013 | 0.0009 | 0.0011 | 0.0016 ^a | 0.0012 |
| | 4 | 0.0006 | 0.0018 | 0.0011 | 0.0025 | 0.0020 | 0.0012 | 0.0012 | 0.0018 ^a |
| | 5 | 0.0016 | 0.0011 | 0.0014 | 0.0024 | 0.0011 | 0.0009 | 0.0014 | 0.0015 |
| | 6 | 0.0004 | 0.0003 | 0.0004 | 0.0004 | 0.0004 | 0.0008 | 0.0004 | 0.0005 |
| | 7 | 0.0002 | 0.0008 | 0.0026 | 0.0023 | 0.0005 | 0.0008 | 0.0011 | 0.0013 |
| | 8 | 0.0008 | 0.0016 | 0.0005 | 0.0011 | 0.0012 | 0.0011 | 0.0008 | 0.0013 |
| | 9 | 0.0007 | 0.0004 | 0.0014 | 0.0017 | 0.0011 | 0.0005 | 0.0011 | 0.0009 |
| | 10 | 0.0004 | 0.0004 | 0.0008 | 0.0012 | 0.0013 | 0.0008 | 0.0008 | 0.0008 |
| | Avg. | 0.0007 | 0.0009 | 0.0013 | 0.0014 | 0.0010 | 0.0009 | 0.0010 | 0.0011 |

Note: Detection limit = $0.0001 \text{ mg}/\text{m}^3$, ND= non detected

PEL and TLV standard of lead = $0.05 \text{ mg}/\text{m}^3$, Thai occupational health standard for lead and its inorganic compound = $0.2 \text{ mg}/\text{m}^3$ and Ambient air quality both Thai and NAAQS standard = $0.0015 \text{ mg}/\text{m}^3$, ^a Over Thai and NAAQS ambient air quality standard

Table 4.17 presents indoor lead particulate concentrations (mg/m^3) collected from Factory B at three different sampling periods and also whole day average. The highest lead concentrations detected on the first floor were 0.0036, 0.0072, and 0.0036 mg/m^3 for each sampling time while detections on the third floor yielded 0.0034, 0.0316, and 0.0031 mg/m^3 for sampling periods 1, 2 and 3, respectively. In this factory, lead-glass heat treatment process is performed within an area which is not separated from the living area; besides, the main ventilation system is poor as it consists only of small vent holes on a side wall. Therefore, from 2.00 to 10.00 am which covers furnace operation period usually performed from 9.00 to 10.00am, lead concentrations are the highest. In addition, hot lead particulate emitted from the furnace can usually disperse to the higher level; consequently, higher lead concentrations were found on the third floor. In comparison with occupational health standards, it is found that indoor lead concentrations both in the first and the third floors at all three sampling periods are still lower than the PEL and TLV standards ($0.05 \text{ mg}/\text{m}^3$) and $0.2 \text{ mg}/\text{m}^3$ of the Thai occupational health standard.

Whole day lead concentrations detected from this factory tend to be higher than the Thai ambient air quality standards and NAAQS ($0.0015 \text{ mg}/\text{m}^3$). Lead concentrations detected on 1st floor fall in the range of $0.0014\text{-}0.0044 \text{ mg}/\text{m}^3$ and on 3rd floor were $0.0010\text{-}0.0126 \text{ mg}/\text{m}^3$.

Although lead concentrations obtained from this factory were below occupational health standards (Thai, PEL, and TLV), concern about long term exposure of the treater and resident should be addressed. Installation of an effective ventilation system within the factory clearly would lead to reduction of lead particulate accumulation within the home factory. In addition, the ruby treatment area should be separated from the living area to reduce lead exposure as much as possible.

Table 4.17 Indoor lead particulate concentrations (mg/m^3) in Factory B at three different sampling periods and whole day average.

| Factory | Sampling time | Indoor lead concentration (mg/m^3) | | | | | | | |
|---------|---------------|--|-----------------------|------------------------------|-----------------------|------------------------------|-----------------------|---------------------------|---------------------------|
| | | Period 1 (6.00pm–2.00am) | | Period 2 (2.00am–10.00am) | | Period 3 (10.00am–6.00pm) | | Whole day (24 hr) | |
| | | 1 st floor | 3 rd floor | 1 st floor | 3 rd floor | 1 st floor | 3 rd floor | 1 st floor | 3 rd floor |
| B | 1 | 0.0011 | 0.0011 | 0.0021 | 0.0016 | 0.0009 | 0.0004 | 0.0014 | 0.0010 |
| | 2 | 0.0017 | 0.0019 | 0.0036 | 0.0051 | 0.0021 | 0.0023 | 0.0025 ^a | 0.0031 ^a |
| | 3 | 0.0018 | 0.0022 | 0.0039 | 0.0054 | 0.0010 | 0.0012 | 0.0022 ^a | 0.0029 ^a |
| | 4 | 0.0007 | 0.0020 | 0.0041 | 0.0223 | 0.0012 | 0.0027 | 0.0020 ^a | 0.0088 ^a |
| | 5 | 0.0036 | 0.0034 | 0.0072 | 0.0309 | 0.0027 | 0.0029 | 0.0044 ^a | 0.0126 ^a |
| | 6 | 0.0006 | 0.0013 | 0.0008 | 0.0021 | 0.0004 | 0.0002 | 0.0006 | 0.0012 |
| | 7 | 0.0034 | 0.0028 | 0.0018 | 0.0083 | 0.0036 | 0.0022 | 0.0029 ^a | 0.0045 ^a |
| | 8 | 0.0016 | 0.0010 | 0.0043 | 0.0176 | 0.0018 | 0.0031 | 0.0026 ^a | 0.0072 ^a |
| | 9 | 0.0019 | 0.0006 | 0.0059 | 0.0316 | 0.0033 | 0.0014 | 0.0037 ^a | 0.0109 ^a |
| | 10 | 0.0012 | 0.0017 | 0.0041 | 0.0282 | 0.0023 | 0.0015 | 0.0025 ^a | 0.0108 ^a |
| | Avg. | 0.0018 | 0.0018 | 0.0038 | 0.0153 | 0.0019 | 0.0018 | 0.0025^a | 0.0063^a |

Note: PEL and TLV standard of lead = $0.05 \text{ mg}/\text{m}^3$, Thai occupational health standard for lead and its inorganic compound = $0.2 \text{ mg}/\text{m}^3$

and Ambient air quality both Thai and NAAQS standard = $0.0015 \text{ mg}/\text{m}^3$

^a Over Thai and NQAAS ambient air quality standard

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Emission Profile

Lead particulate was emitted from the furnace at significant levels due to gate opening (changing step between soaking and cooling periods). This indicated that the furnaces were closed systems and there was no other exit of lead except the furnace gate. During each treatment, the treater spends a short time collecting the ruby from the furnace. This open gate period is not longer than 10 min and the gate is tightly closed all other times. Therefore, lead concentration emission registers highest during the first 10 min after gate opening. Air samples taken in the next 50 minutes indicate very low amount of lead dispersing around the furnace. The important factor affecting the amount of lead emission was the weight of lead additive used in the process. Higher weight of lead additive yields higher amounts of lead emission as reported in the last chapter.

5.2 Estimations of Lead Additive and Emission

5.2.1 Estimation of Lead Additive

This equation can be applied to estimate amount of lead additive used in each treatment.

$$y = 15.586x + 15.622$$

where y is weight of lead additive (g) and x is lead emission concentration (mg/m³) from the monitoring data. Estimation error from the equation falls within the range of 11%.

Normally, amount of lead-glass additives is the top secret of each factory. The goal of this equation is to estimate the overall amount of lead additive imported into Chanthaburi province and used in ruby heat treatment process.

5.2.2 Estimation of Lead Emission

Three equations are constructed to predict the amount of lead emission when various weights of ruby are known:

$$y = 2.229x - 1.992$$

$$y = 4.597x - 4.597 \quad \text{and}$$

$$y = 4.384x - 3.819$$

where x is weight of ruby (kg) used in the treatment and y is estimated lead concentration emission (mg/m^3).

These equations are not suitable to use for prediction of lead emission when less than 2 kg ruby is loaded for treatment. The first equation seems to be more suitable to use to predict lead emission for smaller loads with an average error of 45%. On the other hand, the last two equations are likely more suitable to predict only high weight ruby loading. Lower estimation error is obtained when they are applied to 3 to 5 kg ruby heat treatment (less than 30%); however, the average estimation error from both equations may reach 250%, for low amounts of ruby (lower than 3 kg).

5.3 Exposure of Treater to Lead Particulate

Both the mixing step and gate opening period of the ruby treatment process are the main periods of lead exposure to the treater. Personal lead exposure during opening period are higher than those detected in mixing step for all trials of ruby treatment. These concentrations were higher than the $0.2 \text{ mg}/\text{m}^3$ Thai occupational health standard recommended by Interior Ministry, Thailand and the international occupational health standard $0.05 \text{ mg}/\text{m}^3$ of PEL (OSHA) and $0.05 \text{ mg}/\text{m}^3$ TLV (ACGIH and NIOSH). In conclusion, higher amounts of lead additive added into the process appear to emit higher amounts of lead to the treater. Considering the long term negative health effects of lead, the treaters should always wear a lead particulate trapping mask during work even when small amounts of ruby are treated.

Regarding whole day lead concentrations exposed to the treater at Factory A and lead concentrations detected during resident time of the treater at Factory B, they were significantly lower to the treater than ruby treatment activities and less than Thai ($0.05 \text{ mg}/\text{m}^3$), PEL ($0.05 \text{ mg}/\text{m}^3$) and TLV ($0.05 \text{ mg}/\text{m}^3$) occupational health standard. However, they normally exceed Thai ambient air quality standard ($0.0015 \text{ mg}/\text{m}^3$) as recommended by Pollution Control Department (PCD), Ministry of Natural Resource and Environment, Thailand and NAAQS ($0.0015 \text{ mg}/\text{m}^3$) as set by U.S.EPA. In addition, a more effective ventilation system would rid the

rooms of lead particulate and reduce its exposure to the treater working within these home factories.

5.4 Indoor Lead Particulate in Ruby-Treatment Home Factory

There is no organization that has set the standard for lead for indoor air quality; therefore, the occupational health standard including Thai (0.2 mg/m^3) set by Interior Ministry, Thailand, PEL (0.05 mg/m^3) recommended by OSHA, and TLV (0.05 mg/m^3) which set by ACGIH and NIOSH were used to compared with 8-hr monitoring data. In addition ambient air quality standard for lead (0.0015 mg/m^3) which has been set by Pollution Control Department (PCD), Ministry of Natural Resource and Environment, Thailand and U.S.EPA were used to compare with whole day lead concentration in this study.

Indoor lead concentration within two background home businesses (i.e., internet café and restaurant) and also those obtained from Factory A are much lower than that allowable by both occupational health and ambient air quality standards. However, lead in indoor air from Factory A is about 10 times higher than in the background houses. On the other hand, while lead concentration in Factory B does not exceed either Thai or international occupational health standards; it seems to have high lead concentration all day thus exceeding the ambient air quality standard. The data indicate that ruby heat treatment clearly elevates the concentration of lead within the home factory but providing an efficient ventilation system and separating the treatment area from the living area can reduce the effect of lead from the process.

5.5 Monitoring and Standard

Ruby treatment is quite different from other industrial work because the treater is exposed to very high lead levels for very short periods. This high lead particulate concentration during the mixing step and furnace gate opening period may hugely impact the worker. Generally, industrial standards have been recommended based on exposure over an average 8 hour work day. International occupational health standards (PEL and TLV) recommend 0.05 mg/m^3 during this timeframe. The Thai standard is set at 0.2 mg/m^3 throughout the working time. Based on the results from this study, standards for the ruby treatment industry should not only measure throughout 8 hours but also for the short periods reported here and especially during

the first 10 min after furnace gate opening. After the first 10 min, lead concentrations are mostly below the Thai occupational health standard (0.2 mg/m^3), but the effects of those very high levels in a short time frame and in very close proximity to the treater's face may be far more critical.

Most ruby treatment factories are designed not only as work areas but are also the residence of the treater; therefore, lead indoor standards for this kind of home factory should be set with consideration of the long term health effects on the treater and anyone else who lives in the home factory.



สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

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APPENDICES

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Appendix A

NIOSH 7082 Standard Method

LEAD by Flame AAS

7082

| | | |
|--------------------|---------------------|-----------------------|
| Pb MW: 207.19 (Pb) | CAS: 7439-92-1 (Pb) | RTECS: OF7525000 (Pb) |
| 223.19 (PbO) | 1317-36-8 (PbO) | OG1750000 (PbO) |

METHOD: 7082, Issue 2 EVALUATION: FULL Issue 1: 15 February 1984

Issue 2: 15/8/1994

| | |
|--|---|
| OSHA : 0.05 mg/m ³ | PROPERTIES: soft metal; |
| NIOSH: <0.1 mg/m ³ ; blood Pb 60 µg/100 g | d 11.3 g/cm ³ ; MP 327.5°C valences +2, +4 in salts |
| ACGIH: 0.05 mg/m ³ | |

SYNONYMS: elemental lead and lead compounds except alkyl lead

| SAMPLING | MEASUREMENT |
|---|---|
| SAMPLER: FILTER (0.8-µm MCE) | TECHNIQUE: ATOMIC ABSORPTION SPECTROPHOTOMETER, |
| FLOW RATE: 1 to 4 L/min | FLAME |
| VOL-MIN: 200 L @ 0.05 mg/m ³ | ANALYTE: lead |
| VOL-MAX: 1500 L | ASHING: conc. HNO ₃ , 6 mL + 30% H ₂ O ₂ , 1 mL; 140°C |
| SHIPMENT: routine | FINAL |
| SAMPLE | SOLUTION: 10% HNO ₃ , 10 mL |
| STABILITY: stable | FLAME: air-acetylene, oxidizing |
| BLANKS: 2-10 field blanks/set | WAVELENGTH: 283.3 nm |
| ACCURACY | BACKGROUND D ₂ or H ₂ lamp, or Zeeman |
| RANGE 0.13-0.4 mg/m ³ | CORRECTION Pb ²⁺ in 10% HNO ₃ |
| STUDIED: [1]; 0.15-1.7 mg/m ³ (fume) | CALIBRATION: |
| [2] | RANGE: 10 to 200 µg/sample [2,3] |
| BIAS: 3.10% | ESTIMATED 2.6 µg/sample [4] |
| OVERALL 0.072 [1]; | LOD: |
| PRECISION 0.068 (fume) [2] | PRECISION (ŝ_r): 0.03 [1] |
| (ŝ_rT): | |
| ACCURACY: ± 17.6% | |

APPLICABILITY: The working range is 0.05 to >1 mg/m³ for a 200-L air sample. The method is applicable to elemental lead, including Pb fume, and all other aerosols containing lead. This is an elemental analysis, not compound specific. Aliquots of the samples can be analyzed separately for additional elements.

INTERFERENCES: Use D₂ or H₂ continuum or Zeeman background correction to control flame or molecular absorption. High concentrations of calcium, sulfate, carbonate, phosphate, iodide, fluoride, or acetate can be corrected.

OTHER METHODS: This method combines and replaces P&CAM 173 [3] and S341 [4,5] for lead. Method 7300 (ICP-AES) and 7105 (AAS/GF) are alternate analytical methods. Method 7505 is specific for lead sulfide. The following have not been revised: the dithizone method, which appears in P&CAM 102 [5] and the lead criteria document [6]; and P&CAM 191 (ASV) [7].

REAGENTS:

- 1 Nitric acid, conc.*
- 2 Nitric acid, 10% (v/v). Add 100 mL conc HNO₃ to 500 mL water; dilute to 1 L.
- 3 Hydrogen peroxide, 30% H₂O₂ (w/w), reagent grade.*
- 4 Calibration stock solution, 1000 µg/mL Pb. Commercial standard or dissolve 1.00 g Pb metal in minimum volume of (1+1) HCl and dilute to 1 L with 1% (v/v) HCl. Store in a polyethylene bottle. Stable one year.
- 5 Air, compressed, filtered.
- 6 Acetylene
- 7 Distilled or deionized water.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

- 1 Sampler: Cellulose ester filter, 0.8- m pore size, 37-mm diameter, in cassette filter holder.
- 2 Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
- 3 Atomic Absorption Spectrophotometer with an air-acetylene burner head and background correction.
- 4 Lead hollow cathode lamp or electrode dischargeless lamp.
- 5 Regulators, two-stage, for air and acetylene.
- 6 Beakers, Phillips, 125-mL, or Griffin, 50-mL with watchglass covers.**
- 7 Volumetric flasks, 10- and 100-mL.**
- 8 Assorted volumetric pipets as needed.**
- 9 Hotplate, surface temperature 140 C.
- 10 Bottles, polyethylene, 100-mL.

** Clean all glassware with conc. nitric acid and rinse thoroughly with distilled or deionized water before use.

SPECIAL PRECAUTIONS: Concentrated nitric acid is an irritant and may burn skin. Perform all acid digestions in a fume hood. Hydrogen peroxide is a strong oxidizing agent, a strong irritant, and corrosive to the skin. Wear gloves and eye protection.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 4 L/min for up to 8 h for a total sample size of 200 to 1500 L for TWA measurements. Do not exceed a filter loading of ca. 2 mg total dust.

SAMPLE PREPARATION:

NOTE 1: The following sample preparation gave quantitative recovery (see EVALUATION OF METHOD) [4]. Steps 4 through 9 of Method 7300 or other quantitative ashing techniques may be substituted, especially if several metals are to be determined on a single filter.

NOTE 2: The Appendix gives a microwave digestion procedure which may be necessary for complete recovery of lead from some matrices, especially epoxy-based paint.

3. Open the cassette filter holders and transfer the samples and blanks to clean beakers.
4. Add 3 mL conc. HNO₃, and 1 mL 30% H₂O₂ and cover with a watchglass. Start reagent blanks at this step.

NOTE: If PbO₂ is not present in the sample, the 30% H₂O₂ need not be added [2,4].

5. Heat on 140°C hotplate until volume is reduced to about 0.5 mL.
6. Repeat two more times using 2 mL conc. HNO₃ and 1 mL 30% H₂O₂ each time.
7. Heat on 140°C hotplate until ca. 0.5 mL liquid remains.
8. When sample is dry, rinse the watchglass and walls of the beaker with 3 to 5 mL 10% HNO₃. Allow the solution to evaporate to dryness.
9. Cool each beaker and dissolve the residues in 1 mL conc. HNO₃.
10. Transfer the solution quantitatively to a 10-mL volumetric flask and dilute to volume with distilled water.

NOTE: If the concentration (M) of any of the following is expected to exceed the lead concentration (M) by 10-fold or more, add 1 mL 1 M Na₂EDTA to each flask before dilution to volume: CO₂³⁻, PO₃⁴⁻, I⁻, F⁻, CH₃COO⁻. If Ca²⁺ or SO₂⁴⁻ are present

CALIBRATION AND QUALITY CONTROL:

11. Prepare a series of working standards covering the range 0.25 to 20 µg/mL Pb (2.5 to 200 µg Pb per sample).

- a. Add aliquots of calibration stock solution to 100-mL volumetric flasks. Dilute to volume with 10% HNO₃. Store the working standards in polyethylene bottles and prepare fresh weekly.
 - b. Analyze the working standards together with the blanks and samples (steps 14 and 15).
 - c. Prepare a calibration graph of absorbance vs. solution concentration (µg/mL).
12. Aspirate a standard for every 10 samples to check for instrument drift.
 13. Check recoveries with at least one spiked media blank per 10 samples. Use method of standard additions occasionally to check for interferences.

MEASUREMENT:

14. Set spectrophotometer as specified by the manufacturer and to conditions on page 7082-1.

NOTE: An alternate wavelength is 217.0 nm [8]. Analyses at 217.0 nm have slightly greater sensitivity, but poorer signal-to-noise ratio compared to 283.3 nm. Also, non-atomic absorption is significantly greater at 217.0 nm, making the use of D₂ or H₂ continuum, or Zeeman background correction mandatory at that wavelength.

15. Aspirate standards, samples, and blanks. Record absorbance readings.

NOTE: If the absorbance values for the samples are above the linear range of the standards, dilute with 10% HNO₃, reanalyze, and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

16. Using the measured absorbances, calculate the corresponding concentrations (µg/mL) of lead in the sample, C_s, and average media blank, C_b, from the calibration graph.
17. Using the solution volumes (mL) of the sample, V_s, and media blanks, V_b, calculate the concentration, C (mg/m³), of lead in the air volume sampled, V (L):

$$C = \frac{C_s V_s - C_b V_b}{V}, \text{ mg/m}^3$$

NOTE: µg/mL ≅ mg/m³

EVALUATION OF METHOD:

Method S341 [9] was issued on October 24, 1975, and validated over the range 0.13 to 0.4 mg/3m for a 180-L air sample, using generated atmospheres of lead nitrate [1]. Recovery in the range 18 to 72 µg Pb per sample was 98%, and collection efficiency of 0.8-m mixed

cellulose ester filters (Millipore Type AA) was 100% for the aerosols. Subsequent studies on analytical recovery of 200 µg Pb per sample gave the following results [2,4]:

| <u>Species</u> | <u>Digestion Method</u> | <u>Analytical Recovery, %</u> |
|------------------|--|-------------------------------|
| Pb metal | HNO ₃ only | 92 ± 4 |
| Pb metal | HNO ₃ + H ₂ O ₂ | 103 ± 3 |
| PbO | HNO ₃ only | 93 ± 4 |
| PbS | HNO ₃ only | 93 ± 5 |
| PbO ₂ | HNO ₃ only | 82 ± 3 |
| PbO ₂ | HNO ₃ + H ₂ O ₂ | 100 ± 1 |
| Pb in paint* | HNO ₃ only | 95 ± 6 |
| Pb in paint* | HNO ₃ + H ₂ O ₂ | 95 ± 6 |

*Standard Reference Material #1579, U.S. National Institute of Standards and Technology.

Additional collection efficiency studies were also done using Gelman GN-4 filters for the collection of Pb fume, which had geometric mean diameter of 0.1 µm [2]. Mean collection efficiency for 24 sampling runs at flow rates between 0.15 and 4.0 L/min was > 97 ± 2%. Overall precision, \hat{S}_{RT} , was 0.072 for lead nitrate aerosol [1,9] and 0.068 for Pb fume [2,4].

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METHOD REVISED BY:

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James B. Perkins, David L. Wheeler, and Keith Nicholson, Ph.D., DataChem Laboratories, Salt Lake City, UT, prepared the microwave digestion procedure in the Appendix.

APPENDIX - MICROWAVE DIGESTION FOR LEAD IN PAINT CHIPS (AND OTHER MATRICES)

This procedure is an alternative to the procedure presented in the Sample Preparation section of this method. It provides a rapid, complete acid digestion prior to analysis by flame atomic absorption (FAA), heated graphite furnace atomic absorption (HGFAA), and inductively coupled plasma spectroscopy (ICP) [10].

Apparatus and Material [11-16]

1. Microwave apparatus requirements

- a. The microwave unit provides programmable power with a minimum of 574 W and can be programmed to within ± 10 W of the required power.
- b. The microwave unit cavity is corrosion resistant as well as ventilated. All electronics are protected against corrosion for safe operation.
- c. The system requires Teflon PFA digestion vessels (120-mL capacity) capable of withstanding pressures up to 7.5 ± 0.7 atm (110 ± 10 psi) and capable of controlled pressure relief at pressures exceeding 7.5 ± 0.7 atm (110 ± 10 psi).
- d. A rotating turntable is employed to ensure homogeneous distribution of microwave radiation within the unit. The speed of the turntable should be a minimum of 3 rpm.
- e. A safety concern relates to the use of sealed containers without pressure relief valves in the unit. Temperature is the important variable controlling the reaction. Pressure is needed to attain elevated temperatures but must be safely contained [12].
- f. Polymeric volumetric ware in plastic (Teflon or polyethylene), 50- or 100-mL capacity.
- g. Disposable polypropylene filter funnel.
- h. Analytical balance, 300-g capacity, and minimum ± 0.001 g.

Reagents

1. Nitric acid, concentrated, spectroscopy grade.
2. Reagent Water. Reagent water shall be interference free. All references to water in the method refer to reagent water that meets the ASTM Type 2 standard.

Procedure

1. Calibration of Microwave Equipment

Calibrate microwave equipment in accordance with manufacturer's instructions. If calibration instructions are not available, see EPA Method 3051 [11].

2. All digestion vessels and volumetric ware must be carefully acid washed and rinsed with reagent water. All digestion vessels should be cleaned by leaching with hot (1:1) nitric acid for a minimum of fifteen minutes, rinsed with reagent water, and dried in a clean environment.

3. Sample Digestion

- a. Tare the Teflon PFA digestion vessel.
- b. Weigh out 0.1 g paint chip sample to the nearest 0.001 g into the tared Teflon PFA sample vessel. With large paint chip samples, measure out a 2 cm² piece, weigh to the nearest 0.001 g, and quantitatively transfer it to the vessel.
- c. Add 5.0 ± 0.1 mL concentrated nitric acid to the sample vessel in a fume hood. If a vigorous reaction occurs, allow the reaction to stop before capping the vessel. Cap the vessel and torque the cap to 12 ft-lb (16 N-m) according to the manufacturer's directions.

The sample vessel may be connected to an overflow vessel using Teflon PFA connecting tubes. Place the vessels in the microwave carousel. Connect the overflow vessels to the center well of the unit.

d. Place the vessels evenly distributed in the turntable of the microwave unit using groups of two, six, or 12 sample vessels. Any vessels containing 5 mL of nitric acid for reagent blank purposes are counted as sample vessels. When fewer than the recommended number of samples are to be digested, i.e., three samples plus one blank, the remaining vessels should be filled with 5 mL of nitric acid to achieve the full complement of vessels. This provides an energy balance since the microwave power absorbed is proportional to the total mass in the cavity [14]. Irradiate each group of samples to achieve a temperature of 180 °C in five minutes at a pressure of 50 psi. Continue to irradiate to achieve a temperature of 180 °C at 100 psi after 25 minutes. Continue digestion for five minutes. A sample digestion program for 12 samples is presented in the following table.

PROGRAM VARIABLES FOR PAINT CHIPS SAMPLE DIGESTION WITH NITRIC ACID

| Stage | (1) | (2) | (3) |
|---------------------------|-------|-------|-------|
| Power | 90% | 90% | 0% |
| Pressure, psi | 50 | 100 | 0 |
| Run Time, min | 10:00 | 20:00 | 05:00 |
| Time @ P, min | 05:00 | 15:00 | 00:00 |
| Temperature | 180 C | 180 C | 0 C |
| Fan Speed | 100% | 100% | 100% |
| Number of Vessels: | 12 | | |
| Liquid Volume per Vessel: | 5 mL | | |
| Sample Weight: | 0.1 g | | |

If the analyst wishes to digest other than two, six, or 12 samples at a time, use different values of power as long as they result in the same time and temperature conditions.

e. At the end of the microwave program, allow the vessels to cool for a minimum of five minutes before removing them from the microwave unit. If a loss of sample is detected (e.g., material in overflow collection vessel, liquid outside liner), determine the reason for the loss (e.g., loss of vessel seal integrity, use of a digestion time longer than 30 minutes, too large a sample, or improper heating conditions). Once the source of the loss has been corrected, prepare a new sample beginning at Section 2. If insufficient material is

available for reanalysis, dilute remaining digestate and note that some sample loss may have occurred.

f. Uncap and vent each vessel in a fume hood. Add 20 mL reagent water, then reseal vessels and shake to mix thoroughly. Transfer the sample to an acid-cleaned polyethylene bottle. If the digested sample contains particulates which may clog nebulizers or interfere with injection of the sample into the instrument, allow the sample to settle or filter it:

Settling: Allow the sample to stand until the supernatant is clear (usually, overnight is sufficient). If it does not clear, filter the sample.

Filtering: The filtering apparatus must be thoroughly precleaned and rinsed with dilute nitric acid. Filter the sample through quantitative filter paper into a second acid-cleaned container.

The digestate is now ready for analysis for elements of interest using the appropriate method.

4. Calculations: Report the concentrations based on the actual weight of the original sample.



Appendix B

Whole Day Lead Concentration in Indoor Air

Whole day lead concentration can be calculated by the summation of amount of lead ($\times 10^{-3}$ mg) in all three periods then the results are divided by the summation of air volume (m^3) in all three periods.

Table B.1 Lead mass ($\times 10^{-3}$ mg) detected and air volume (m^3) collected in internet café

| Times | Lead mass ($\times 10^{-3}$ mg) | | | Air volume (m^3) | | | Whole day (24 hour) lead conc. (mg/m^3) |
|-------|----------------------------------|----------|----------|----------------------|----------|----------|---|
| | Period 1 | Period 2 | Period 3 | Period 1 | Period 2 | Period 3 | |
| 1 | 0.303 | 0.429 | 0.201 | 1.443 | 1.430 | 1.439 | 0.0002 |
| 2 | 0.553 | 0.803 | 0.320 | 1.495 | 1.434 | 1.456 | 0.0004 |
| 3 | 0.079 | 0.073 | 0.100 | 1.385 | 1.452 | 1.431 | 0.0001 |
| 4 | 0.174 | 0.145 | 0.078 | 1.450 | 1.447 | 1.361 | 0.0001 |
| 5 | 0.436 | 0.578 | 0.433 | 1.482 | 1.472 | 1.502 | 0.0003 |

Table B.2 Lead mass ($\times 10^{-3}$ mg) detected and air volume (m^3) collected in Restaurant

| Times | Lead mass ($\times 10^{-3}$ mg) | | | Air volume (m^3) | | | Whole day (24 hour) lead conc. (mg/m^3) |
|-------|----------------------------------|----------|----------|----------------------|----------|----------|---|
| | Period 1 | Period 2 | Period 3 | Period 1 | Period 2 | Period 3 | |
| 1 | 0.044 | 0.060 | 0.044 | 1.474 | 1.494 | 1.480 | ND |
| 2 | 0.044 | 0.064 | 0.043 | 1.466 | 1.273 | 1.428 | ND |
| 3 | 0.058 | 0.101 | 0.059 | 1.446 | 1.439 | 1.471 | ND |
| 4 | 0.116 | 0.058 | 0.084 | 1.450 | 1.441 | 1.392 | ND |
| 5 | 0.029 | 0.059 | 0.101 | 1.431 | 1.472 | 1.448 | ND |

Note: ND = non detected

Table B.3 Lead mass ($\times 10^{-3}$ mg) detected and air volume (m^3) collected in the first and third floor of Factory A

| Times | 1 st floor | | | | | | | 3 rd floor | | | | | | |
|-------|----------------------------------|----------|----------|-----------------------------|----------|----------|---|----------------------------------|----------|----------|-----------------------------|----------|----------|---|
| | Lead mass ($\times 10^{-3}$ mg) | | | Air volume (m^3) | | | Whole day (24 hr) lead conc. (mg/m^3) | Lead mass ($\times 10^{-3}$ mg) | | | Air volume (m^3) | | | Whole day (24 hr) lead conc. (mg/m^3) |
| | Period 1 | Period 2 | Period 3 | Period 1 | Period 2 | Period 3 | | Period 1 | Period 2 | Period 3 | Period 1 | Period 2 | Period 3 | |
| 1 | 0.060 | 0.014 | 0.030 | 1.491 | 1.439 | 1.480 | ND | 0.028 | 0.072 | 0.044 | 1.383 | 1.443 | 1.480 | ND |
| 2 | 0.876 | 2.309 | 2.522 | 1.460 | 1.443 | 1.401 | 0.0013 | 2.460 | 1.628 | 1.936 | 1.447 | 1.357 | 1.383 | 0.0014 |
| 3 | 1.769 | 3.871 | 1.344 | 1.444 | 1.434 | 1.494 | 0.0016 | 1.819 | 1.933 | 1.646 | 1.400 | 1.487 | 1.497 | 0.0012 |
| 4 | 0.862 | 1.569 | 2.773 | 1.437 | 1.426 | 1.387 | 0.0012 | 2.646 | 3.745 | 1.726 | 1.470 | 1.498 | 1.439 | 0.0018 |
| 5 | 2.313 | 2.095 | 1.589 | 1.446 | 1.496 | 1.444 | 0.0014 | 1.635 | 3.466 | 1.244 | 1.486 | 1.444 | 1.382 | 0.0015 |
| 6 | 0.556 | 0.573 | 0.509 | 1.391 | 1.433 | 1.436 | 0.0004 | 0.415 | 0.581 | 1.168 | 1.384 | 1.452 | 1.460 | 0.0005 |
| 7 | 0.288 | 3.748 | 0.750 | 1.439 | 1.441 | 1.500 | 0.0011 | 1.159 | 3.302 | 1.182 | 1.449 | 1.436 | 1.478 | 0.0013 |
| 8 | 1.171 | 0.730 | 1.725 | 1.464 | 1.460 | 1.437 | 0.0008 | 2.385 | 1.643 | 1.574 | 1.491 | 1.494 | 1.431 | 0.0013 |
| 9 | 1.002 | 2.048 | 1.641 | 1.432 | 1.463 | 1.492 | 0.0011 | 0.553 | 2.490 | 0.747 | 1.383 | 1.464 | 1.494 | 0.0009 |
| 10 | 0.588 | 1.157 | 1.881 | 1.471 | 1.446 | 1.447 | 0.0008 | 0.598 | 1.730 | 1.191 | 1.495 | 1.441 | 1.489 | 0.0008 |

Note: ND = non detected

Table B.4 Lead mass ($\times 10^{-3}$ mg) detected and air volume (m^3) collected in the first and third floor of Factory B

| Times | 1 st floor | | | | | | | 3 rd floor | | | | | | |
|-------|----------------------------------|----------|----------|-----------------------------|----------|----------|---|----------------------------------|----------|----------|-----------------------------|----------|----------|---|
| | Lead mass ($\times 10^{-3}$ mg) | | | Air volume (m^3) | | | Whole day (24 hr) lead conc. (mg/m^3) | Lead mass ($\times 10^{-3}$ mg) | | | Air volume (m^3) | | | Whole day (24 hr) lead conc. (mg/m^3) |
| | Period 1 | Period 2 | Period 3 | Period 1 | Period 2 | Period 3 | | Period 1 | Period 2 | Period 3 | Period 1 | Period 2 | Period 3 | |
| 1 | 1.450 | 2.950 | 1.390 | 1.376 | 1.380 | 1.497 | 0.0014 | 1.530 | 2.130 | 0.591 | 1.437 | 1.365 | 1.433 | 0.0010 |
| 2 | 2.470 | 5.410 | 2.950 | 1.446 | 1.495 | 1.379 | 0.0025 | 2.780 | 7.550 | 3.470 | 1.443 | 1.471 | 1.490 | 0.0031 |
| 3 | 2.580 | 5.660 | 1.480 | 1.407 | 1.441 | 1.488 | 0.0022 | 3.180 | 7.810 | 1.780 | 1.441 | 1.442 | 1.482 | 0.0029 |
| 4 | 0.960 | 6.150 | 1.750 | 1.468 | 1.498 | 1.453 | 0.0020 | 2.770 | 30.810 | 4.040 | 1.388 | 1.382 | 1.491 | 0.0088 |
| 5 | 5.370 | 9.870 | 3.840 | 1.494 | 1.379 | 1.439 | 0.0044 | 4.820 | 46.150 | 4.170 | 1.439 | 1.495 | 1.447 | 0.0126 |
| 6 | 0.870 | 1.180 | 0.558 | 1.376 | 1.489 | 1.441 | 0.0006 | 1.860 | 3.150 | 0.332 | 1.466 | 1.476 | 1.414 | 0.0012 |
| 7 | 4.830 | 2.570 | 5.320 | 1.436 | 1.437 | 1.480 | 0.0029 | 3.860 | 12.380 | 3.020 | 1.389 | 1.498 | 1.384 | 0.0045 |
| 8 | 2.390 | 6.420 | 2.480 | 1.449 | 1.482 | 1.391 | 0.0026 | 1.490 | 25.420 | 4.580 | 1.494 | 1.446 | 1.460 | 0.0072 |
| 9 | 2.720 | 8.490 | 4.820 | 1.462 | 1.432 | 1.440 | 0.0037 | 0.910 | 44.190 | 2.060 | 1.463 | 1.400 | 1.463 | 0.0109 |
| 10 | 1.780 | 5.870 | 3.280 | 1.454 | 1.444 | 1.443 | 0.0025 | 2.420 | 42.150 | 2.200 | 1.383 | 1.497 | 1.434 | 0.0109 |

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