



**UNIVERSITI PUTRA MALAYSIA**

***HEAVY METALS IN THE TOBACCO OF COMMERCIAL AND DO IT  
YOURSELF (DIY) CIGARETTE AND ITS HEALTH RISK***

**CALVIN LADIUS**

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YOURSELF (DIY) CIGARETTE AND ITS HEALTH RISK**

**BY**

**CALVIN LADIUS**

**This thesis submitted in fulfilment of the requirement for the degree of Bachelor  
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## ABSTRACT

### HEAVY METALS IN THE TOBACCO OF COMMERCIAL AND DO IT YOURSELF (DIY) CIGARETTE AND ITS HEALTH RISK

Calvin Ladius, Sharifah Norkhadijah Syed Ismail, Emilia Zainal Abidin

Department of Environmental and Occupational Health, Faculty of Medicine and Health Science, University Putra Malaysia, 43400 Serdang, Selangor

**Introduction:** Cigarette smoking is one of the major causes of morbidity and mortality in the world. Heavy metals are one of the toxic element found in tobacco smoke which can accumulate in the body tissues and fluids. Increase of excise tax and price of the commercial cigarette have caused smokers to shift from smoking commercial cigarette to do it yourself (DIY) cigarette. **Objective:** To determine the concentration and health risk of heavy metals in the tobacco of commercial and DIY cigarette. **Methodology:** Purposive sampling of 24 tobacco samples (16 commercial and 8 DIY cigarette) selected based on the type, flavor and price. The samples were oven dried (48 hours), grinded and sieved (250um) before analyzed. The prepared samples were analyzed using XRF technique. **Results:** Commercial cigarette was detected with high Fe ( $1155.81 \pm 212.25$  mg/kg) followed by Mn ( $398.13 \pm 84.52$  mg/kg), Cu ( $36.11 \pm 9.50$  mg/kg), Pb ( $0.63 \pm 0.94$  mg/kg), Hg ( $0.21 \pm 0.46$  mg/kg) and As ( $0.03 \pm 0.07$  mg/kg). Meanwhile, the DIY tobacco was detected with high Zn ( $79.61 \pm 39.27$  mg/kg) followed by Cr ( $40.96 \pm 14.73$  mg/kg) and Ni ( $8.13 \pm 1.46$  mg/kg). Cd was detected with similar range between commercial ( $0.88 \pm 1.67$  mg/kg) and DIY cigarette ( $0.81 \pm 1.51$  mg/kg). Cr ( $p=0.001$ ) and Ni ( $p=0.01$ ) were significantly higher in commercial cigarette. Cu ( $p=0.02$ ), Fe ( $p=0.03$ ), Ni ( $p=0.01$ ) and Pb ( $p=0.02$ ) were significant higher in expensive cigarette. Cr ( $p=0.04$ ) was significantly higher in the cigarette with original flavor. Moderate correlation were detected between As-Pb ( $r=0.57$ ,  $p=0.004$ ), Cd-Pb ( $r=0.484$ ,  $p=0.016$ ), Cr-Mn ( $r=-0.491$ ,  $p=0.015$ ), Cr-Pb ( $r=-0.433$ ,  $p=0.034$ ), Cu-Hg ( $r=0.432$ ,  $p=0.035$ ), Mn-Ni ( $r=-0.575$ ,  $p=0.003$ ), Mn-Pb ( $r=0.414$ ,  $p=0.044$ ), and Ni-Pb ( $r=-0.579$ ,  $p=0.003$ ). While there was a high correlation detected between Cr-Ni ( $r=0.845$ ,  $p=0.00$ ) No risk of non-carcinogenic detected through ingestion and inhalation for all heavy metals. There were significant carcinogenic risk of developing 1 cancer per 1000000 population for Cr (risk= $7.38 \times 10^{-6}$ ) and Ni (risk= $2.01 \times 10^{-6}$ ) through ingestion. **Conclusion:** There were some heavy metals concentration that were found significantly different by types, prices and flavors. There were also some heavy metals concentration that have a significant relationship with other heavy metals. There are no non-carcinogenic risk but there are carcinogenic risk posed by heavy metals in the tobacco of commercial and DIY cigarette. Although there was no significant non-carcinogenic risk, heavy metals were found in the cigarette. Further study is recommended to assess the actual risk of heavy metals exposure in cigarette to the Malaysian population.

**Keywords:** Cigarette, tobacco, heavy metals, health risk.

## ABSTRAK

### LOGAM BERAT DALAM TEMBAKAU ROKOK KOMERSIL DAN ROKOK BUAT SENDIRI DAN RISIKO KESIHATAN

Calvin Ladius, Sharifah Norkhadijah Syed Ismail, Emilia Zainal Abidin

Jabatan Kesihatan Persekitaran dan Pekerjaan, Fakulti Perubatan dan Sains Kesihatan, Universiti Putra Malaysia, 43400 Serdang, Selangor

**Pengenalan:** Merokok merupakan salah satu punca utama kesan kesihatan dan kematian di dunia. Logam berat adalah salah satu elemen toksik yang boleh dijumpai dalam asap rokok dan boleh berkumpul di dalam tisu dan cecair badan. Kenaikan cukai dan harga rokok komersial menyebabkan perokok beralih daripada menghisap rokok komersial kepada rokok buat sendiri untuk menjimatkan kos. **Objektif:** Untuk menentukan kandungan dan risiko kesihatan logam berat dalam tembakau rokok komersial dan rokok buat sendiri. **Metodologi:** 24 sampel tembakau (16 rokok komersial dan 8 rokok buat sendiri) dipilih berdasarkan jenis, rasa dan harga. Sampel telah diletakkan dalam ketuhar sehingga kering (48 jam), dikisar dan diayak (250 $\mu$ m) sebelum dianalisis. Sampel kemudiannya dianalisis dengan menggunakan teknik x-ray fluorescence. **Keputusan:** Rokok komersial dikesan dengan Fe tinggi (1155,81  $\pm$  212,25 mg/kg) diikuti oleh Mn (398,13  $\pm$  84.52 mg/kg), Cu (36.11  $\pm$  9.50 mg/kg), Pb (0.63  $\pm$  0.94 mg/kg), Hg (0.21  $\pm$  0.46 mg/kg) dan As (0.03  $\pm$  0.07 mg/kg). Tembakau buat sendiri pula dikesan dengan Zn tinggi (79.61  $\pm$  39.27 mg/kg) diikuti oleh Cr (40,96  $\pm$  14.73 mg/kg) dan Ni (8.13  $\pm$  1.46 mg/kg). Cd dikesan sama antara tembakau komersial (0.88  $\pm$  1.67 mg/kg) dan tembakau buat sendiri (0.81  $\pm$  1.51 mg/kg). Cr (p=0.001) dan Ni (p=0.01) dikesan lebih tinggi dalam tembakau komersial. Cu (p=0.02), Fe (p=0.03), Ni (p=0.01) dan Pb (p = 0.02) lebih tinggi dalam rokok mahal. Cr (p=0.04) adalah lebih tinggi dalam rokok perisa asli. Terdapat hubungan sederhana antara As-Pb (r=0.57, p=0.004), Cd-Pb (r=0,484, p=0.016), Cr-Mn (r=-0,491, p=0.015), Cr-Pb (r=-0,433, p=0.034), Cu-Hg (r=0,432, p=0.035), Mn-Ni (r=-0,575, p=0.003), Mn-Pb (r=0,414, p=0,044), dan Ni-Pb (r=-0,579, p=0.003). Terdapat hubungan tinggi antara Cr-Ni (r=0,845, p=0.00). Tiada risiko bukan karsinogen dikesan melalui pemakanan dan pernafasan untuk semua logam berat. Risiko karsinogenik dikesan untuk Cr (risk=4.34 x 10<sup>1</sup>) and Ni (risk=1.91 x 10<sup>1</sup>) untuk mengakibatkan 1 kanser setiap 1000000 penduduk melalui pemakanan. **Kesimpulan:** Terdapat kepekatan logam berat yang jauh berbeza dengan jenis, harga dan perisa rokok. Terdapat juga kepekatan logam berat yang mempunyai hubungan signifikan dengan logam berat lain. Tiada risiko kesihatan bukan karsinogen tetapi terdapat risiko kesihatan karsinogen untuk logam berat yang terdapat dalam tembakau rokok komersial dan rokok buat sendiri. Walaupun tiada signifikan risiko bukan karsinogen, tetapi logam berat dikesan di dalam sample rokok. Kajian pada masa hadapan disarankan agar risiko pendedahan kepada logam berat dalam rokok di kalangan rakyat Malaysia dapat ditentukan.

**Kata kunci:** Rokok, tembakau, logam berat, risiko kesihatan.

## TABLE OF CONTENTS

|   |      |
|---|------|
| DECLARATION   | i    |
| ACKNOWLEDGEMENTS  | iii  |
| ABSTRACT  | ii   |
| ABSTRAK   | iii  |
| TABLE OF CONTENTS   | iv   |
| LIST OF TABLES  | vi   |
| LIST OF FIGURES   | vii  |
| LIST OF ABBREVIATIONS                                       | viii |
| CHAPTER 1: INTRODUCTION                                     | 1    |
| 1.1 Background  | 1    |
| 1.2 Problem statements                                      | 3    |
| 1.3 Research justification                                  | 4    |
| 1.4 Conceptual framework                                    | 5    |
| 1.5 Research objectives and hypothesis                      | 7    |
| 1.5.1 General objective                                     | 7    |
| 1.5.2 Specific objective                                    | 7    |
| 1.5.3 Hypothesis  | 7    |
| CHAPTER 2: LITERATURE REVIEW                                | 8    |
| 2.1 Types of tobacco  | 8    |
| 2.3 Commercial and do it yourself (DIY) cigarette           | 10   |
| 2.3 Cigarette and its components                            | 12   |
| 2.4 Mechanism of heavy metals                               | 13   |
| 2.5 Sources of heavy metals contamination in tobacco leaves | 15   |
| 2.6 Passage from tobacco cigarette to smoke                 | 16   |

|  |    |
|--|----|
| 2.7 Cigarette taxes  | 17 |
| CHAPTER 3: METHODOLOGY   | 19 |
| 3.1 Sample collection  | 19 |
| 3.2 Sample preparation   | 21 |
| 3.3 Sample analysis  | 22 |
| 3.4 Health risk assessment   | 23 |
| 3.5 Statistical analysis   | 27 |
| CHAPTER 4: RESULTS AND DISCUSSIONS   | 28 |
| 4.1 Comparison of heavy metals by type, price and flavor                             | 28 |
| 4.2 Correlation between heavy metals   | 33 |
| 4.3 Determination of non-carcinogenic and carcinogenic health risk                   | 34 |
| 4.4 Discussion on the comparison of heavy metals by types, prices and flavors        | 37 |
| 4.5 Discussion on the correlation between heavy metals                               | 39 |
| 4.6 Discussion on the determination of non-carcinogenic and carcinogenic health risk | 40 |
| CHAPTER 5: CONCLUSION  | 44 |
| CHAPTER 6: LIMITATION AND RECOMMENDATION   | 45 |
| 6.1 Limitation of study  | 45 |
| 6.2 Recommendation   | 46 |
| REFERENCES   | 47 |

## LIST OF TABLES

|              |   | <b>Page</b> |
|--------------|---|-------------|
| Table 2.7    | Cigarette taxes in Malaysia from 1990 to 2010           | 17          |
| Table 3.1    | List of tobacco samples                                 | 21          |
| Table 3.4.1a | Variables used in equations                             | 24          |
| Table 3.4.1b | Reference dose (RfD) for non-carcinogenic risk          | 25          |
| Table 3.4.1c | Reference concentration (RfC) for non-carcinogenic risk | 25          |
| Table 3.4.2a | Variables used in equation                              | 26          |
| Table 3.4.2b | Cancer slope factor (CSF)                               | 27          |
| Table 3.4.2c | Unit risk factor (URF)                                  | 27          |
| Table 4.1    | Comparison of heavy metals by cigarette types           | 30          |
| Table 4.2    | Comparison of heavy metals by cigarette prices          | 31          |
| Table 4.3    | Comparison of heavy metals by cigarette flavors         | 32          |
| Table 4.4    | Correlation between heavy metals                        | 33          |
| Table 4.5    | Non-carcinogenic risk                                   | 35          |
| Table 4.6    | Carcinogenic risk                                       | 36          |

## LIST OF FIGURES

|                      |  | <b>Page</b> |
|----------------------|--|-------------|
| Figure 1.4.1         | Conceptual framework of research                         | 6           |
| Figure 2.3a          | Commercial cigarette in box package                      | 10          |
| Figure 2.3b          | Commercial cigarette stick                               | 10          |
| Figure 2.3c          | Do it yourself cigarette                                 | 11          |
| Figure 2.3d          | Do it yourself cigarette (local-made tobacco from Sabah) | 11          |
| Figure 2.3e          | Do it yourself cigarette in box package                  | 11          |
| Figure 3.1           | Flow chart for methodology                               | 19          |
| Figure 3.1a          | Commercial cigarette                                     | 20          |
| Figure 3.1b          | Do It Yourself cigarette                                 | 20          |
| Figure 3.2a          | Oven dried   | 22          |
| Figure 3.2b          | Grinding sample  | 22          |
| Figure 3.2c          | Sieving sample   | 22          |
| Figure 3.3           | XOS HD-Rocksand  | 23          |
| Figure 3.3b,<br>3.3c | Analysis of samples by XOS HD-Rocksand                   | 23          |

## LIST OF ABBREVIATIONS

|         |   |
|---------|---|
| ADD     | Average daily dose  |
| As      | Arsenic   |
| ATSDR   | Agency for Toxic Substances & Disease Registry              |
| Cal EPA | California Environmental Protection Agency                  |
| Cd      | Cadmium   |
| Cr      | Chromium  |
| Cu      | Copper  |
| DIY     | Do it yourself  |
| Fe      | Iron  |
| Hg      | Mercury   |
| IARC    | International Agency for Research on Cancer                 |
| IRIS    | Integrated Risk Information System                          |
| LADD    | Lifetime average daily dose                                 |
| Mn      | Manganese   |
| Ni      | Nickel  |
| OEHHA   | California Office of Environmental Health Hazard Assessment |
| Pb      | Lead  |
| RfC     | Reference concentration                                     |
| RfD     | Reference dose  |
| US EPA  | United State Environmental Protection Agency                |
| WHO     | World Health Organization                                   |
| XRF     | X-ray fluorescence  |
| Zn      | Zinc  |

## CHAPTER 1

### INTRODUCTION

#### 1.1 Background

The consumption of tobacco products and number of smokers have been increasing steadily all over the world. The use of cigarettes constitutes one of the major causes of morbidity and mortality in the world. Tobacco smoke has toxic, genotoxic, and carcinogenic properties. The cigarette smoke contains both organic and inorganic human carcinogenic compounds. More than 7000 chemicals (hydrocarbons, aldehydes, ketones, aromatic hydrocarbons, heavy metals including lead and arsenic) have been isolated from tobacco which over 20 are probably carcinogenic and over 60 mutagenic (International Agency for Research on Cancer (IARC), 2004). These toxic materials are heavy metals, particularly cadmium and lead which enters through inhalation route and might increase the vulnerability of lung tissues to radiation. Lead and arsenic have been identified and measured both in tobacco and tobacco smoke which indicates that cigarette smoke is very harmful and toxic for human health (IARC, 2004).

Smoking-related diseases are ultimately the result of nicotine addiction (U.S. Department of Health and Human Services, 2010), which leads to the repeated inhalation of a variety of toxicants in cigarette smoke, including nitrosamines, polycyclic aromatic hydrocarbons, volatile organic compounds, and several toxic

heavy metals (Talhout et al., 2011). Among these toxicants, there have been comparatively fewer studies conducted on the role of heavy metals as causes of smoking-related diseases and there is a need for basic studies on the levels of heavy metals in cigarettes and other tobacco products.

The presence of trace amounts of metals in tobacco smoke has been known for some time (Verma, Yadav, & Singh, 2010). Those most commonly associated with health effects include arsenic (As), cadmium (Cd), chromium (Cr), nickel (Ni), and lead (Pb). As, Cd, and Cr (VI), as well as Ni compounds, are all categorized as carcinogenic heavy metals to humans (Fowles & Dybing, 2003).

The level of exposure to metals in the smoke drawn from a single cigarette is small and likely not acutely toxic, but the accumulation of metals in the body over months, years, and decades of exposure is, depending on clearance rates, a health concern (Behera, Xian, & Balasubramanian, 2014). Several heavy metals found in tobacco smoke, such as Cd, Cr, Pb, and Ni, accumulate in tissues and fluids after smoking (Galażyn-Sidorczuk, Brzóska, & Moniuszko-Jakoniuk, 2007). This is a particular issue for Cd and Pb, which have long (10–12 year) half-lives in the human body. Cigarette smoking is a major exposure route for Cd in the general population (Richter, Bishop, Wang, & Swahn, 2009).

Human population is exposed to lead and arsenic from many sources (air, water, soils, foodstuffs, and anthropogenic sources). Smoking is not the main source of lead exposure for humans, but cigarette smoking influences lead and arsenic

toxicity. However, bio-monitoring studies show that smokers have substantially higher Cd and Pb levels (Richter et al., 2009).

In the tobacco plantation herbicides, insecticides, and fungicides are used to control the various parasites and plant diseases. Metals enter the tobacco plant during growing dominantly by absorption from soil and from the application of fertilizers, with uptake rate influenced by soil pH (Pelit, Demirdöğen, & Henden, 2013).

## **1.2 Problem statements**

Consumption of tobacco is the major cause of morbidity and mortality in the world. This is caused by the component present in tobacco which are hydrocarbons, aldehydes, ketones, aromatic hydrocarbons, heavy metals that could cause toxic and carcinogenic effects to human (IARC, 2004).

The report from Global Adult Tobacco Survey in Malaysia in 2011 shows that there is high prevalence of adult male smokers compared to female adult smokers. Smoking prevalence in 2011 of adult males in Malaysia was measured at 43.9% while smoking prevalence of adult females in Malaysia was measured at 1% (Lim et al., 2013). The high number of male smokers (43.9%) is alarming the government to do control and mitigating measures as to reduce the number of people who smoke and second-hand smokers exposed to tobacco smoke.

An article from New Straits Times, (2015) stated that the prices of cigarette in Malaysia have increases up to 40%. The increased in prices of cigarette have causes

smokers to shift from smoking commercial cigarette to do it yourself (DIY) cigarette to cut some cost. With lack of hygienic practice, smokers who rolled their own cigarette in DIY were exposed to contaminants or heavy metals in the tobacco. Study about heavy metals in cigarette is widely conducted, however there are limited studies done to determine the risk of heavy metals exposure via tobacco used in DIY cigarette. According to the World Health Organization Study Group on Tobacco Product Regulation (TobReg), further studies are required to determine the concentrations of metals in the cigarette tobacco (Fowles & Dybing, 2003), in order to supplement current knowledge on the physical transport of heavy metals into smoke.

### **1.3 Research justification**

The main justification to carry out this study is because of high number of adult Malaysian male (43.9% prevalence) are smokers (Lim et al., 2013). Besides that, there are increasing number of people especially young people in our country that taking up smoking habit. These indirectly denote exposure to community which could lead to increase number of smokers in the future. The amount of heavy metals in the tobacco of cigarette will be relate to the development of cardiovascular problems to the chronic smokers (Higgins et al., 2016).

This research could provide information to complement limited studies focus on the concentration of heavy metals in different type of tobacco in DIY cigarette. Because of lacking in the study pertaining to it, it may affect this study being failed to see the potential of tobacco as the one agent for heavy metals exposure and its chronic effect. Therefore, it becomes the role of this study to prove that the tobacco in

commercial cigarette and DIY cigarette contain significant level of heavy metals which could cause health problems to the community affected.

#### **1.4 Conceptual framework**

This conceptual framework shows the independent and dependent variables of this research. The independent variables are type, price and flavor. The dependent variables are heavy metal concentration and health risk. This conceptual framework illustrates how the type, prices and flavor of tobacco could affect the concentration and health risk of the heavy metals.

Heavy metals are found to be present in the tobacco of cigarette. The concentration of heavy metals depends on the type, price and flavor of tobacco (Gilmore, Tavakoly, Hiscock, & Taylor, 2015). Other cofounder which could affect heavy metal concentration are through occupational (manufacturing and agriculture) and environmental (water, soil and air) settings. These heavy metals in tobacco could interacts with humans through 3 types of exposure which are dermal contact, inhalation and ingestion. This could lead to carcinogenic health risk such as cancer or non-carcinogenic health risk such as respiratory problem (Behera et al., 2014).

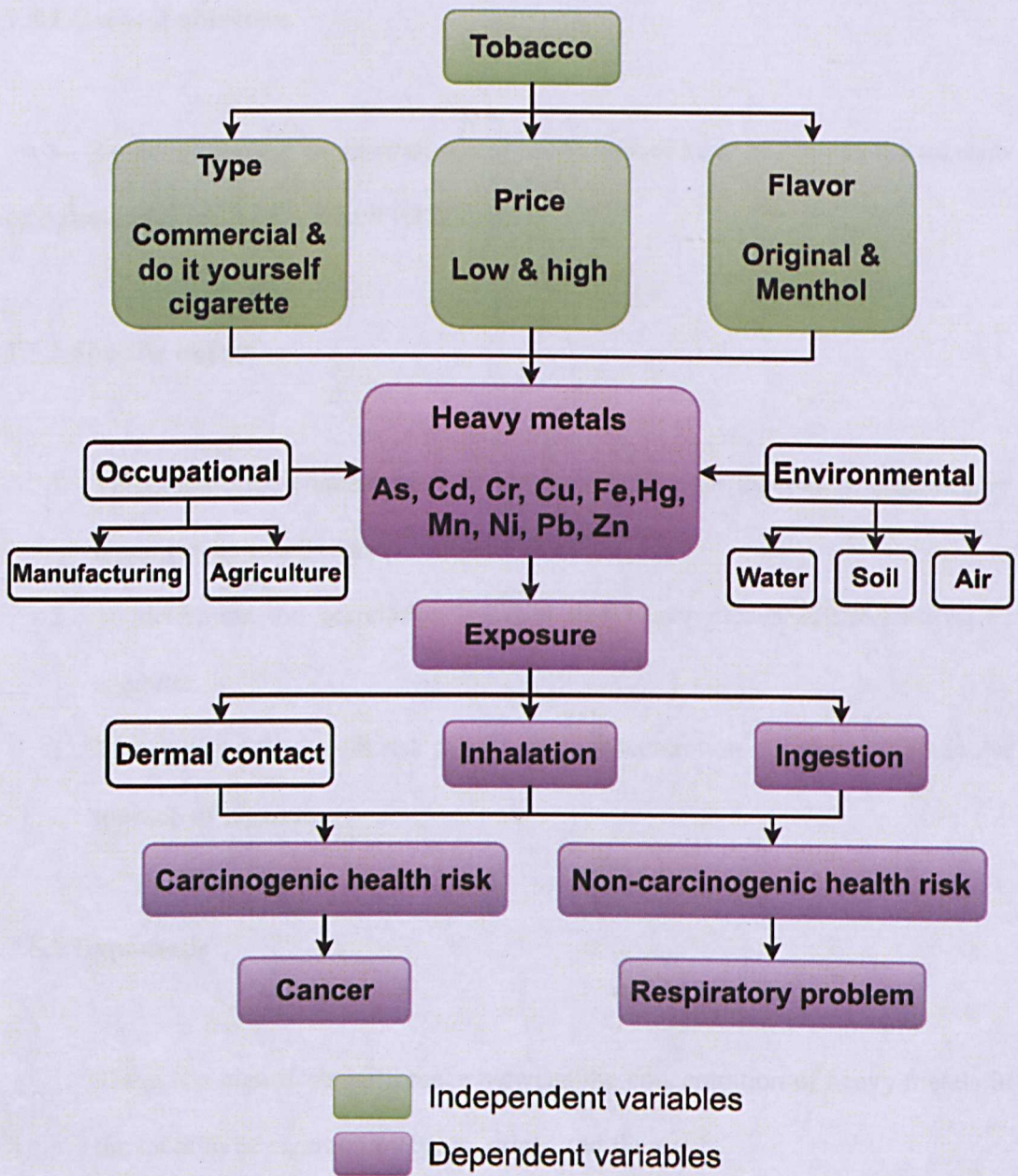


Figure 1.4.1: Conceptual framework of study

## **1.5 Research objectives and hypothesis**

### **1.5.1 General objective**

To determine the concentration and health risk of heavy metals in the tobacco of commercial and do it yourself (DIY) cigarette.

### **1.5.2 Specific objective**

1. To compare the concentration of heavy metals in the tobacco of cigarette by types, prices and flavors.
2. To determine the correlation between two heavy metals in the tobacco of cigarette.
3. To determine the health risk poses by the concentration of heavy metals in the tobacco of cigarette.

### **1.5.3 Hypothesis**

1. There is a significant difference between the concentration of heavy metals in the tobacco of cigarette by types, prices and flavors.
2. There is a correlation between the concentration of heavy metals in the tobacco of cigarette.
3. There is a significant health risk posed by the heavy metals in the tobacco of cigarette

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Types of tobacco

Many kinds of tobacco are grown in the world, with a variety of uses. The types of tobacco vary according to tobacco classes in various countries and elements such as manipulation of nitrogen fertilization, plant density, time and height of topping, harvesting and curing are added to favorably influence the usability of the cured leaves for specific products (Geiss & Kotzias, 2007).

Virginia includes 40% of world tobacco production. Virginia is high in sugar and low in oils. The color of the leaves ranges from bright lemon yellow to medium brown, the lighter colors being spicier in flavor and the darker colored leaves having a deeper and complex taste. Some of the heavier leaves may be used in mixtures for pipe smoking. Some English cigarettes are entirely composed of Virginia tobacco. Major producers of Virginia tobacco in the world are China, USA, Brazil, India and Zimbabwe (Geiss & Kotzias, 2007).

Burley includes 11% of world production. It is high in oil, low in sugar and has a nutty type of flavor. Burley is usually light air-cured, derived from the White Burley which arose as a mutant on a farm in Ohio in 1864. Some of the heavier leaves are used in pipe blends and also for chewing. Cured burley leaf is characterized by low sugar content and a very low sugar to nitrogen ratio (high nicotine). This is

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enhanced by high amounts of nitrogen-fertilizers, harvesting at an early stage of senescence, and the air curing process allows for oxidation of any sugar which may have occurred. Main producers of burley tobacco in the world are U.S.A., Italy, Korea, Brazil and Mexico (Geiss & Kotzias, 2007).

Maryland includes only small total of world production. It is a neutral type of tobacco with a mild flavor. Maryland is another usually light air-cured type. It is used in some American blended cigarettes and to a greater extent in certain Swiss cigarette blends. Maryland tobacco is extremely fluffy, has good burning properties, low nicotine and a neutral aroma. Main production countries are USA and Italy (Geiss & Kotzias, 2007).

Oriental includes 16% of total production. Oriental tobacco is mild with a very characteristic aroma. Resins, waxes and gum exuded by glandular hairs (trichomes) supply the aroma. Nicotine is low, averaging around 1%. The tobacco is usually sun-cured. Main production countries are Russia, Turkey, Bulgaria, Greece, Serbia, Romania and Italy (Geiss & Kotzias, 2007).

Nicotiana Rustica were introduced when the first settlers reached Jamestown, Virginia. They found the Native Americans smoking Nicotiana Rustica which contains about 10% nicotine. Over the following 300 years, Rustica lost a lot of ground to Nicotiana Tabacum. Nowadays Rustica is grown and used in India, Pakistan, Bangladesh, Russia, Indonesia, Afghanistan, Burma, Iran, Iraq, Algeria, Africa and South America. Nicotiana Rustica is smoked primarily in water pipes but is occasionally smoked in cigarettes or chewed (Geiss & Kotzias, 2007).

### 2.3 Commercial and do it yourself (DIY) cigarette

A cigarette is defined as any roll of tobacco wrapped in paper or other non-tobacco material (Benjakul et al., 2013). Cigarettes are approximately 8 mm in diameter and 70–120 mm in length. Cigarette can be either commercially manufactured or individually made. The most common tobacco product in developed countries is the commercial cigarette which is also known as manufactured cigarette. Definition provided by GATS Malaysia, 2011 stated that commercial cigarette is a product composed of a small dried and minced tobacco portion, rolled in thin paper and manufactured (Mohd Yusoff, Guat Hiong, Singh, & Kuang Hock, 2011).



Figure 2.3a: Commercial cigarette in box package



Figure 2.3b: Commercial cigarette stick

Do it yourself (DIY) cigarette also known as roll your own (RYO) cigarette are referred to the cigarettes made by hand-rolled using shredded tobacco and papers (Benjakul et al., 2013). This cigarette is a cheaper substitute for commercially manufactured cigarette brand and are gaining in popularity worldwide. DIY cigarettes are typically less expensive than commercial cigarette (factory manufactured) and serve as a discount option for smokers (Young et al., 2008). DIY smoking was associated with people living in rural areas, older age, lower level of education, male smokers, not working and lower attitude towards regulations (Young et al., 2008).



Figure 2.3c: Do it yourself cigarette



Figure 2.3d: Do it yourself cigarette  
(local-made tobacco from Sabah)



Figure 2.3e: Do it yourself cigarette  
in box packages

## 2.3 Cigarette and its components

Cigarette is one of the means by which trace elements in tobacco is made available for human consumption. Usually, cigarette is made up of tobacco, paper and additives. As much as 600 to 1400 additives are used in cigarette manufacture, with many of these additives containing trace elements (Pourkhabbaz & Pourkhabbaz, 2012).

A study of more than 300 ingredients added to cigarette reported an increase in the yield of total particulate matter (TPM) in the range of 13 to 28% relative to the cigarettes without these ingredients (Rustemeier, Stabbert, Haussmann, Roemer, & Carmines, 2002). This was attributed to a higher transfer rates of the added ingredients to smoke.

Since 1950, the make-up of cigarettes and the consumption of cigarette smoke have gradually changed. This was achieved primarily with the introduction of filter tips (with and without perforation), selection of tobacco types and varieties, utilization highly porous cigarette paper and incorporation into the tobacco blend of reconstituted tobacco and expanded tobacco (Hammond & O'Connor, 2008).

## 2.4 Mechanism of heavy metals

Heavy metals are substances with high electrical conductivity, malleability, and luster, which voluntarily lose their electrons to form cations. Metals are found naturally in the earth's crust and their compositions vary according to different localities, resulting in spatial variations of surrounding concentrations. The metal distribution in the atmosphere is monitored by the properties of the given metal and by various environmental factors (Khlifi & Hamza-Chaffai, 2010).

Arsenic is one of the most important heavy metals from ecological and individual health standpoints. It has a semi-metallic property, toxic and carcinogenic, and is available in the form of oxides or sulfides or as a salt of iron, sodium, calcium, and copper (Singh, Kumar, & Sahu, 2007). Arsenic is the twentieth most abundant element on earth and its inorganic forms such as arsenite and arsenate compounds are lethal to the environment and living creatures. Humans may encounter arsenic by natural means, industrial source, or from unintended sources.

Lead is a bright silvery metal, slightly bluish in a dry atmosphere. It begins to tarnish on contact with air, thereby forming a complex mixture of compounds, depending on the given conditions. The sources of lead exposure include mainly industrial processes, food and smoking, drinking water and domestic sources. The sources of lead were gasoline and house paint, which has been extended to lead bullets, plumbing pipes, pewter pitchers, storage batteries, toys and faucets (Galażyn-Sidorczuk et al., 2007).

Mercury is a naturally occurring metal which is a shiny silver-white, odorless liquid and becomes colorless and odorless gas when heated. Mercury is very toxic and exceedingly bio-accumulative. Its presence adversely affects the marine environment and hence many studies are directed towards the distribution of mercury in water environment. Major sources of mercury pollution include anthropogenic activities such as agriculture, municipal wastewater discharges, mining, incineration, and discharges of industrial wastewater (Chen, Chen, & Dong, 2012).

Cadmium is the seventh most toxic heavy metal as per ATSDR ranking. It is a by-product of zinc production which humans or animals may get exposed at work or from the environment. Once this metal gets absorbed by humans, it will accumulate inside the body throughout life. It is also being used in rechargeable batteries, for special alloys production and also present in tobacco smoke. About three-fourths of cadmium is used in alkaline batteries as an electrode component, the remaining part is used in coatings, pigments, plating and as a plastic stabilizer. Humans may get exposed to this metal primarily by inhalation and ingestion and can suffer from acute and chronic intoxications (He et al., 2013).

Chromium is the seventh most abundant element on earth. The most commonly occurring forms are trivalent and hexavalent chromium, with both being toxic to animals, humans and plants (Kimura, 2007). Chromium occurs naturally by the burning of oil and coal, petroleum from refractory material, pigment oxidants, catalyst, chromium steel, fertilizers, oil well drilling and metal plating tanneries. Anthropogenically, chromium is released into the environment through sewage and fertilizers (Tchounwou, Yedjou, Patlolla, & Sutton, 2012).

Iron is the second most abundant metal on the earth's crust. Iron is a most crucial element for growth and survival of almost all living organisms. It is one of the vital components of organisms like algae and of enzymes such as cytochromes and catalase, as well as of oxygen transporting proteins, such as hemoglobin and myoglobin. The source of iron is related to anthropogenic work and mining activities (Valko, Morris, & Cronin, 2005).

## 2.5 Sources of heavy metals contamination in tobacco leaves

Previous study reported that tobacco is fast growing, deep-rooted, easily propagated, has a high biomass production and hyper-accumulators, ability to extract, accumulate and tolerate high levels of heavy metals from soils (Alkorta et al., 2004; Robinson et al., 2000). In Canada, the contents of such metals in cigarette tobacco have been determined as an indicator of environmental change (Hammond & O'Connor, 2008).

Levels of heavy metals in tobacco are higher when grown in soil contaminated with heavy metal. Environmental factors which may influence heavy metal uptake by tobacco plants including soil pH and heavy metal-containing sludge or fertilizers applied to crops. Toxic metals found in these soils cause deleterious effects due to inhalation of contaminated soil, or from the ingestion of fruits and vegetables grown in contaminated soils. There have been research stated that uptake of metals by plants depends on the physico-chemical makeup of the plant species and soil (Samsøe-Petersen, Larsen, Larsen, & Bruun, 2002).

Hyper accumulator plants are able to accumulate high amounts of heavy metals in their tissues, at concentrations 10 to 100 times higher than those tolerated by crop plants. Over 450 plant species have been identified as hyper accumulators of trace metals (Zn, Ni, Mn, Cu, Co, and Cd), metalloids and nonmetals elements (Verbruggen, Hermans, & Schat, 2009).

## 2.6 Passage from tobacco cigarette to smoke

Elements pass from tobacco to smoke and smoke condensate (the so-called tar). Cigarette filters succeed in retaining only a proportion of the elements concentration. Environmental smoke pollution consists not only of smoke exhaled by the smokers but also of side stream smoke emitted by the burning cigarette (Geiss & Kotzias, 2007).

Side stream smoke, which is inhaled by non-smokers (secondhand smokers), usually contains relatively high concentration of many noxious substances including heavy metals. As particle sizes are smaller in side stream smoke than in mainstream smoke, their deposition in the lung tissue of passive smokers reaches deeper into the alveolar spaces (Geiss & Kotzias, 2007).

## 2.7 Cigarette taxes

As for year 2012, the excise tax on cigarette is 49% or 26 sen per stick of the retail price which is still lower than 70% suggested by Frame Convention on Tobacco Control (FCTC), 2009. Cigarette tax is collected from cigarette manufacturers or cigarette importers. Until 2004, taxes on tobacco were levied according to their weight. In 2005, Malaysia has adopted a specific excise tax per stick and this tax structure is easier to administer since it requires only counting the sticks without weighing them. Table 2.7 shows the cigarette taxes imposed by the Malaysia government from 1990 until 2010. Both the excise tax and import tax imposed on cigarettes are increasing however, the sales tax remains fixed at 15% from 1990 to 1999 and increase to 25% from 2001 to 2010 (Ross & Al-Sadat, 2007).

Table 2.7: Cigarette taxes in Malaysia from 1990 to 2010

| Year      | Import tax<br>(RM/kg or RM/stick) | Nominal excise tax<br>(RM/kg or RM/stick) | Sales tax<br>(%) |
|-----------|-----------------------------------|---|------------------|
| 1990      | 85/0.08                           | 13/0.013                                  | 15               |
| 1991      | 135/0.12                          | 14/0.014                                  | 15               |
| 1992-1998 | 162/0.15                          | 28.60/0.028                               | 15               |
| 1999-2000 | 180/0.16                          | 40/0.039                                  | 15               |
| 2001      | 180/0.16                          | 40/0.039                                  | 25               |
| 2002      | 216/0.2                           | 48/0.047                                  | 25               |
| 2003      | 259/0.24                          | 58/0.056                                  | 25               |
| 2004      | 200/0.18                          | 58/0.056                                  | 25               |
| 2005*     | 0.20                              | 0.081                                     | 25               |
| 2006      | 0.20                              | 0.12                                      | 25               |
| 2007      | 0.20                              | 0.15                                      | 25               |
| 2008      | 0.2                               | 0.18                                      | 25               |
| 2009      | 0.2                               | 0.225                                     | 25               |
| 2010      | 0.2                               | 0.26                                      | 25               |

\*Specific tax per stick was introduced (1 kg = 1100 sticks)

Source: Royal Custom Malaysia and Confederation of Malaysia Tobacco (CMTM)

The Malaysian Government earns a large amount of revenue from its involvement in the tobacco industry. In 2010, revenue from the excise tax on cigarette is 2% from the total revenue of excise tax collected by the government. It is estimated that an increase of 10% in cigarette tax would lead to an increase almost 7% in government revenue (World Bank 1999). Previous study predicted that the impact of a 25% increase in cigarette excise tax in Malaysia would result 20.8% increase in cigarette tax revenue (Ross & Al-Sadat, 2007).

There are several reasons for raising cigarette excise taxes such as; to increase government revenue, to protect children and youth, to improve public health and to correct externalities. These entire reasoning further pose a question as to what is the optimal tax that should be imposed on cigarette. From the economic perspective, the optimal tax can be achieved when the marginal cost of the last cigarette consumed equals to its marginal social benefits. However, according to previous study, evaluation and identification of the negative externalities associated with direct smoking and direct environmental effect from tobacco smoke are abundant and complicated (Levy, Benjakul, Ross, & Ritthiphakdee, 2008; Ross & Al-Sadat, 2007). Therefore for a country to set the level of tax, it should take into account the national health objectives and also depends on societal value such as the extent to which the children should be protected from the effect of smoke polluted environment.

## CHAPTER 3

### METHODOLOGY

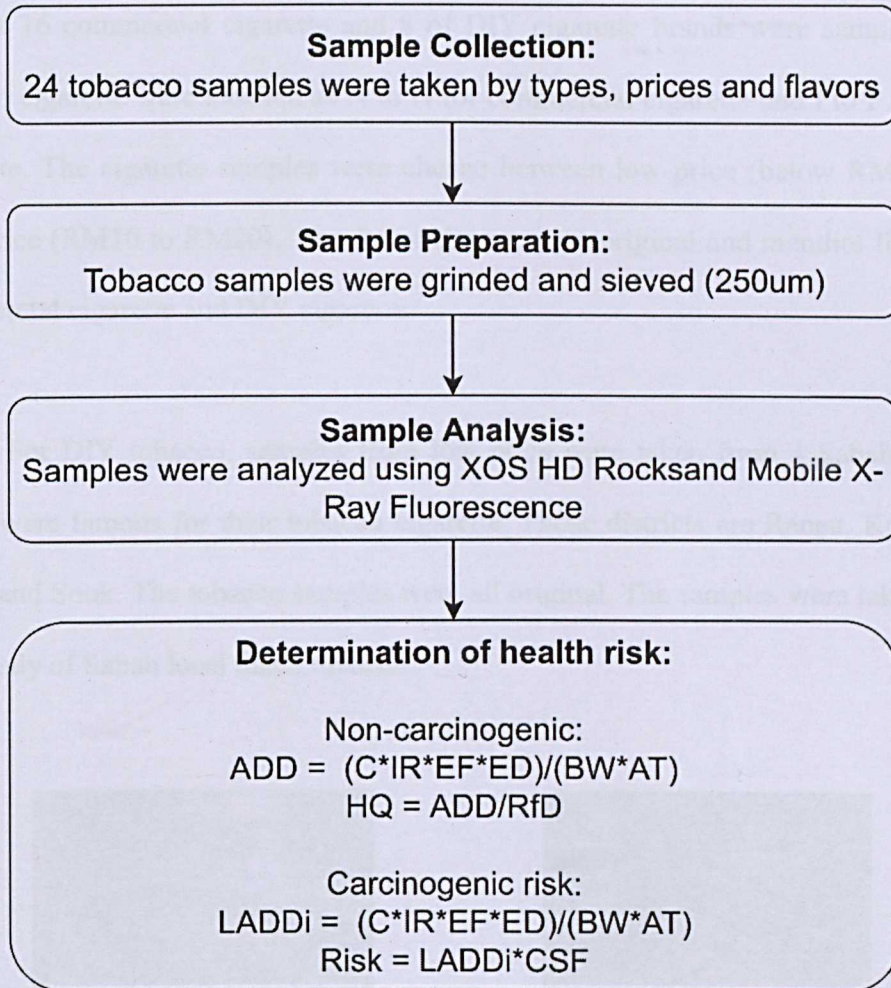


Figure 3.1: Flow chart for methodology

### 3.1 Sample collection

Sample of cigarette was collected on the month of January, 2016. Commercial and DIY cigarette were selected based on the brands (most common brand in the market), types (original and menthol) and prices (low and high price). Tobacco from a total of 16 commercial cigarette and 8 of DIY cigarette brands were sampled. The tobacco cigarette were labelled as A to H for commercial cigarette and I to P for DIY cigarette. The cigarette samples were chosen between low price (below RM10) and high price (RM10 to RM20). The flavor chosen were original and menthol flavor for commercial cigarette and DIY cigarette.

For DIY tobacco, samples from low price were taken from 4 Sabah district which were famous for their tobacco cigarette. Those districts are Ranau, Keningau, Kudat and Sook. The tobacco samples were all original. The samples were taken for a case study of Sabah local made tobacco.



Figure 3.1a: Commercial cigarette



Figure 3.1b: Do It Yourself cigarette

Table 3.1: List of tobacco sample

| Price                            | Flavor   | Commercial cigarette sample | DIY cigarette sample |
|----------------------------------|----------|-----------------------------|----------------------|
| High price<br>(RM10 to<br>RM20)  | Original | A1                          | I                    |
|                                  |          | B1                          | J                    |
|                                  |          | C1                          | K                    |
|                                  |          | D1                          | L                    |
|                                  | Menthol  | A2                          |                      |
|                                  |          | B2                          |                      |
|                                  |          | C2                          | -                    |
|                                  |          | D2                          |                      |
| Low Price<br>(RM10 and<br>below) | Original | E1                          | M                    |
|                                  |          | F1                          | N                    |
|                                  |          | G1                          | O                    |
|                                  |          | H1                          | P                    |
|                                  | Menthol  | E2                          |                      |
|                                  |          | F2                          |                      |
|                                  |          | G2                          | -                    |
|                                  |          | H2                          |                      |

### 3.2 Sample preparation

All of the samples were oven dried for 48 hours to make sure that samples are completely dried. After removing from oven, the samples were immediately grinded so that it can be easily break down to smaller size and to prevent it from being expose to air. After grinding process, the samples were filtered using a sieve with a size of 250um. The sieved samples were put into a transparent sterile plastic bag (Stephens & Calder, 2004).



Figure 3.2a: Oven dried



Figure 3.2b: Grinding sample

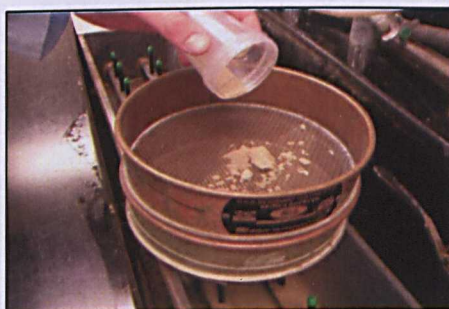


Figure 3.2c: Sieving sample

### 3.3 Sample analysis

Samples were analyzed using a portable x-ray fluorescence device (XOS HD Rocksand Mobile 1.2.6 IOP-M2 10WPS S7 4SS). It is widely used for environmental, industrial, pharmaceutical, forensic, and scientific research applications to determine the presence or absence and in some cases to measure the concentration of elemental constituents or contaminants. The fluorescing atoms can be excited by energetic electrons, ions, or photons. The level of detection is in part per million (ppm). The samples in the transparent sterile plastic bag were put inside the machine and were analyzed for 6 minutes. The readings were presented in an excel form. Standard method taken from (Stephens & Calder, 2004).



Figure 3.3: XOS HD-Rocksand



Figure 3.3b and 3.3c: Analysis of samples by XOS HD-Rocksand

### 3.4 Health risk assessment

#### 3.4.1 Non-carcinogenic health risk

The average daily dose (ADD) was calculated for the non-carcinogenic risk as follows:

$$ADD = \frac{C \times IR \times EF \times ED}{BW \times AT}$$

Table 3.4.1a: Variables used in equations

| Parameter                                | Value                              | Unit      | Source                            |
|--|------------------------------------|-----------|-----------------------------------|
| C = Average concentration of heavy metal | Depend on results of this research | mg/kg     | Based on results of this research |
| IR = Ingestion rate                      | 50                                 | mg/day    | US EPA                            |
| IR = Inhalation rate                     | 20                                 | m3/day    | US EPA                            |
| EF = Exposure frequency                  | 365                                | days/year | US EPA                            |
| ED = Exposure duration                   | 30                                 | years     | US EPA                            |
| BW = Body weight                         | 70                                 | kg        | US EPA                            |
| AT = Average period of exposure (ED*365) | 10950                              | days      | US EPA                            |

US EPA = United State Environmental Protection Agency

For non-carcinogenic risk, hazard quotient (HQ) >1 indicates significant risk while HQ<1 indicates no significant risk. The HQ and reference dose used in the calculation were as follow:

$$\text{For ingestion, HQ} = \frac{\text{ADD}}{\text{Rfd}}$$

$$\text{For inhalation, HQ} = \frac{\text{ADD}}{\text{RfC}}$$

Table 3.4.1b: Reference dose (RfD) for non-carcinogenic risk

| Heavy metals | Reference dose, RfD (mg/kg-d) | Source  |
|--------------|-------------------------------|---------|
| As           | 0.0003                        | US EPA  |
| Cd           | 0.001                         | US EPA  |
| Cr           | 1.5                           | US EPA  |
| Cu           | 0.04                          | US EPA  |
| Fe           | 0.7                           | US EPA  |
| Hg           | 0.00016                       | Cal EPA |
| Mn           | 0.14                          | US EPA  |
| Ni           | 0.02                          | US EPA  |
| Pb           | 0.0036                        | US EPA  |
| Zn           | 0.3                           | US EPA  |

US EPA = United State Environmental Protection Agency

Cal EPA = California Environmental Protection Agency

Table 3.4.1c: Reference concentration (RfC) for non-carcinogenic risk

| Heavy metals | Reference concentration, RfC (mg/m <sup>3</sup> ) | Source  |
|--------------|---|---------|
| As           | 0.000015  | Cal EPA |
| Cd           | 0.00001   | ATSDR   |
| Cr           | 0.0001  | IRIS    |
| Cu           | -   | -       |
| Fe           | -   | -       |
| Hg           | 0.0003  | ATSDR   |
| Mn           | 0.00005   | IRIS    |
| Ni           | 0.00009   | ATSDR   |
| Pb           | -   | -       |
| Zn           | -   | -       |

ATSDR = Agency for Toxic Substances & Disease Registry

Cal EPA = California Environmental Protection Agency

IRIS = Integrated Risk Information System

### 3.4.2 Carcinogenic health risk

The Lifetime Average Daily Dose (LADDi) is used to calculate the carcinogenic risk. LADDi were as follows:

$$LADDi = \frac{C \times IR \times EF \times ED}{BW \times AT}$$

Table 3.4.2a: Variables used in equation

| Subject                                  | Value                              | Unit                | Source                            |
|--|------------------------------------|---------------------|-----------------------------------|
| C = Average concentration of heavy metal | Depend on results of this research | mg/kg               | Based on results of this research |
| IR = Ingestion rate                      | 50                                 | mg/day              | US EPA                            |
| IR = Inhalation rate                     | 20                                 | m <sup>3</sup> /day |                                   |
| EF = Exposure frequency                  | 365                                | days/year           | US EPA                            |
| ED = Exposure duration                   | 30                                 | years               | US EPA                            |
| BW = Body weight                         | 70                                 | kg                  | US EPA                            |
| AT = Average period of exposure (70*365) | 25550                              | days                | US EPA                            |

US EPA = United State Environmental Protection Agency

Risk between  $1 \times 10^{-6}$  and  $1 \times 10^{-4}$  is considered not acceptable. There is a significant risk if exceed  $1 \times 10^{-6}$ . The carcinogenic risk were as follow:

For ingestion, Risk = LADDi x CSF

For inhalation, Risk = LADDi x URF

Table 3.4.2b: Cancer slope factor (CSF)

| Heavy metals | Cancer slope factor, CSF |       |
|--------------|--------------------------|-------|
|              | (mg/kg-d)                |       |
| As           | 1.5                      | OEHHA |
| Cd           | 1.5                      | OEHHA |
| Cr           | 0.5                      | OEHHA |
| Ni           | 0.91                     | OEHHA |

OEHHA = California Office of Environmental Health Hazard Assessment

Table 3.4.2c: Unit risk factor (URF)

| Heavy metals | Unit risk factor, URF   |      |
|--------------|-------------------------|------|
|              | (mg/ m <sup>3</sup> -d) |      |
| As           | 0.0043                  | IRIS |
| Cd           | 0.0018                  | IRIS |
| Cr           | 0.084                   | IRIS |
| Ni           | 0.00024                 | IRIS |

IRIS = Integrated Risk Information System

### 3.5 Statistical analysis

Data were analyzed using IBM SPSS version 22. The differences between the concentration of heavy metals based on types, prices and flavors of cigarette were analyzed using Independent T-test and Mann Whitney-U test. The relationship between the concentrations of two heavy metals in the tobacco of cigarette were analyzed using Pearson Correlation and Spearman Correlation test.

## CHAPTER 4

### RESULTS AND DISCUSSION

#### 4.1 Comparison of heavy metals concentration by type, price and flavor

A total of 24 cigarette samples by types (commercial and DIY), price (low and high) and flavor (original and menthol) were analyzed for heavy metals (As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb and Zn). All heavy metals were detected in the tobacco samples except for As, Cd, Hg and Pb.

The commercial cigarette were detected with high Fe ( $1155.81 \pm 212.25$  mg/kg), followed by Mn ( $398.13 \pm 84.52$  mg/kg), Cu ( $36.11 \pm 9.50$  mg/kg), Pb ( $0.63 \pm 0.94$  mg/kg), Hg ( $0.21 \pm 0.46$  mg/kg) and As ( $0.03 \pm 0.07$  mg/kg). Meanwhile, the DIY tobacco were detected with high Zn ( $79.61 \pm 39.27$  mg/kg), Cr ( $40.96 \pm 14.73$  mg/kg) and Ni ( $8.13 \pm 1.46$  mg/kg). Cd was detected at similar range between commercial ( $0.88 \pm 1.67$  mg/kg) and DIY cigarette ( $0.81 \pm 1.51$  mg/kg) (Table 4.1).

Fe was significantly higher ( $1067.75 \pm 316.62$  mg/kg) ( $t=2.058$ ,  $p=0.049$ ) in the commercial cigarette compared to the DIY while Cr ( $28.36 \pm 14.57$  mg/kg) ( $t=-3.747$ ,  $p=0.001$ ) and Ni ( $6.85 \pm 1.83$  mg/kg) ( $t=-2.702$ ,  $p=0.01$ ) were significantly higher in the DIY cigarette compared to the commercial one (Table 4.1). Other elements were not difference by cigarette types.

Cu ( $33.97 \pm 9.63$  mg/kg) ( $t=2.34$ ,  $p=0.02$ ), Fe ( $1067.75 \pm 316.62$  mg/kg) ( $t=2.058$ ,  $p=0.03$ ) and Ni ( $6.85 \pm 1.83$  mg/kg) ( $t=-2.702$ ,  $p=0.01$ ) were significantly higher in expensive tobacco compared to the cheap one except for Pb ( $0.46 \pm 0.82$  mg/kg) ( $t=1.398$ ,  $p=0.02$ ) where it was significantly high in cheap tobacco. Other elements were not significantly difference by price (Table 4.2).

Only Cr was significantly higher ( $t=2.20$ ,  $p=0.04$ ) in original flavor tobacco with the mean  $\pm$  SD of ( $28.36 \pm 14.57$  mg/kg) while other elements were not significantly difference by flavor (Table 4.3).

Table 4.1: Comparison of heavy metals by cigarette types

(Commercial N=16, DIY N=8)

| Heavy metals | Type       | Sample detected | Range (mg/kg)  | Mean $\pm$ SD (mg/kg) | t / U  | p-value |
|--------------|------------|-----------------|----------------|-----------------------|--------|---------|
| As           | Commercial | 2               | 0 - 0.2        | 0.03 $\pm$ 0.07       | N/A    | N/A     |
|              | DIY        | 0               | ND             | ND                    |        |         |
| Cd           | Commercial | 4               | 0 - 5.0        | 0.88 $\pm$ 1.67       | 0.098  | 0.92    |
|              | DIY        | 2               | 0 - 3.4        | 0.81 $\pm$ 1.51       |        |         |
| Cr           | Commercial | 16              | 12.10 - 50.9   | 22.07 $\pm$ 9.88      | -3.747 | *0.001  |
|              | DIY        | 8               | 24.2 - 63.3    | 40.96 $\pm$ 14.73     |        |         |
| Cu           | Commercial | 16              | 24.5 - 52.5    | 36.11 $\pm$ 9.50      | 1.590  | 0.13    |
|              | DIY        | 8               | 23.4 - 50.8    | 29.69 $\pm$ 8.96      |        |         |
| Fe           | Commercial | 16              | 879.0 - 1581.0 | 1155.81 $\pm$ 212.25  | 2.058  | *0.049  |
|              | DIY        | 8               | 382.0 - 1427.0 | 891.63 $\pm$ 423.90   |        |         |
| Hg           | Commercial | 3               | 0 - 1.5        | 0.21 $\pm$ 0.46       | 0.435  | 0.67    |
|              | DIY        | 1               | 0 - 1.0        | 0.13 $\pm$ 0.35       |        |         |
| Mn           | Commercial | 16              | 278.0 - 566.0  | 398.13 $\pm$ 84.52    | 0.219  | 0.83    |
|              | DIY        | 8               | 239.0 - 1008.0 | 382.88 $\pm$ 256.60   |        |         |
| Ni           | Commercial | 16              | 3.8 - 9.5      | 6.22 $\pm$ 1.70       | -2.702 | *0.01   |
|              | DIY        | 8               | 6.4 - 10.6     | 8.13 $\pm$ 1.46       |        |         |
| Pb           | Commercial | 6               | 0 - 2.7        | 0.63 $\pm$ 0.94       | 1.398  | 0.18    |
|              | DIY        | 1               | 0 - 1.1        | 0.14 $\pm$ 0.39       |        |         |
| Zn           | Commercial | 16              | 56.8 - 80.7    | 71.10 $\pm$ 6.57      | -0.862 | 0.40    |
|              | DIY        | 8               | 49.2 - 166.0   | 79.61 $\pm$ 39.27     |        |         |

ND = Not detected

N/A = Not available

t = Independent t-test

U = Mann-Whitney U test

\*There is a significant difference when  $p < 0.05$

Table 4.2: Comparison of heavy metals by cigarette prices

(Low n=12, High n=12)

| Heavy metals | Price | Sample detected | Range (mg/kg)  | Mean $\pm$ SD (mg/kg) | t / U | p-value |
|--------------|-------|-----------------|----------------|-----------------------|-------|---------|
| As           | Low   | 2               | 0 - 0.2        | 0.03 $\pm$ 0.08       | N/A   | N/A     |
|              | High  | 0               | ND             | ND                    |       |         |
| Cd           | Low   | 4               | 0 - 5.0        | 1.25 $\pm$ 1.92       | -1.22 | 0.24    |
|              | High  | 2               | 0 - 3.4        | 0.47 $\pm$ 1.12       |       |         |
| Cr           | Low   | 12              | 14.6 - 47.2    | 24.39 $\pm$ 10.43     | 1.36  | 0.19    |
|              | High  | 12              | 12.1 - 63.3    | 32.34 $\pm$ 17.35     |       |         |
| Cu           | Low   | 12              | 23.4 - 50.8    | 29.76 $\pm$ 7.22      | 2.34  | *0.03   |
|              | High  | 12              | 24.3 - 52.5    | 38.18 $\pm$ 10.16     |       |         |
| Fe           | Low   | 12              | 382.0 - 1320.0 | 930.42 $\pm$ 330.09   | 2.31  | *0.03   |
|              | High  | 12              | 879.0 - 1581.0 | 1205.08 $\pm$ 243.94  |       |         |
| Hg           | Low   | 1               | 0 - 1.0        | 0.08 $\pm$ 0.29       | 1.11  | 0.28    |
|              | High  | 3               | 0 - 1.5        | 0.28 $\pm$ 0.52       |       |         |
| Mn           | Low   | 12              | 263.0 - 1008.0 | 448.42 $\pm$ 192.89   | -1.80 | 0.08    |
|              | High  | 12              | 239.0 - 566.0  | 337.67 $\pm$ 88.63    |       |         |
| Ni           | Low   | 12              | 3.8 - 8.9      | 5.98 $\pm$ 1.50       | 2.59  | *0.02   |
|              | High  | 12              | 4.1 - 10.6     | 7.73 $\pm$ 1.78       |       |         |
| Pb           | Low   | 6               | 0 - 2.7        | 0.83 $\pm$ 1.01       | -2.43 | *0.02   |
|              | High  | 1               | 0 - 1.1        | 0.09 $\pm$ 0.32       |       |         |
| Zn           | Low   | 12              | 46.8 - 166.0   | 80.73 $\pm$ 29.66     | -1.50 | 0.15    |
|              | High  | 12              | 49.2 - 80.7    | 67.15 $\pm$ 9.77      |       |         |

ND = Not detected

N/A = Not available

t = Independent T-test

U = Mann-Whitney U test

\*There is a significant difference when  $p < 0.05$

Table 4.3: Comparison of heavy metals by cigarette flavors

(Original n=16, Menthol n=8)

| Heavy metals | Price    | Sample detected | Range (mg/kg)  | Mean $\pm$ SD (mg/kg) | t / U | p-value |
|--------------|----------|-----------------|----------------|-----------------------|-------|---------|
| As           | Original | 0               | ND             | ND                    | N/A   | N/A     |
|              | Menthol  | 2               | 0 - 0.2        | 0.05 $\pm$ 0.09       |       |         |
| Cd           | Original | 3               | 0 - 4.1        | 0.66 $\pm$ 1.44       | -0.84 | 0.41    |
|              | Menthol  | 3               | 0 - 5.0        | 1.25 $\pm$ 1.90       |       |         |
| Cr           | Original | 16              | 12.1 - 63.3    | 32.66 $\pm$ 16.01     | 2.20  | *0.04   |
|              | Menthol  | 8               | 14.6 - 29.3    | 19.79 $\pm$ 4.79      |       |         |
| Cu           | Original | 16              | 23.4 - 52.5    | 32.78 $\pm$ 9.97      | -0.85 | 0.40    |
|              | Menthol  | 8               | 25.0 - 46.1    | 36.35 $\pm$ 9.08      |       |         |
| Fe           | Original | 16              | 382.0 - 1556.0 | 1027.06 $\pm$ 354.03  | -0.88 | 0.39    |
|              | Menthol  | 8               | 958.0 - 1581.0 | 1149.13 $\pm$ 222.40  |       |         |
| Hg           | Original | 2               | 0 - 1.0        | 0.13 $\pm$ 0.34       | -0.88 | 0.39    |
|              | Menthol  | 2               | 0 - 1.5        | 0.29 $\pm$ 0.56       |       |         |
| Mn           | Original | 16              | 239.0 - 1008.0 | 392.13 $\pm$ 181.75   | -0.03 | 0.97    |
|              | Menthol  | 8               | 278.0 - 566.0  | 394.88 $\pm$ 102.65   |       |         |
| Ni           | Original | 16              | 3.8 - 10.6     | 7.16 $\pm$ 2.05       | 1.14  | 0.26    |
|              | Menthol  | 8               | 4.6 - 8.0      | 6.25 $\pm$ 1.21       |       |         |
| Pb           | Original | 4               | 0 - 2.4        | 0.37 $\pm$ 0.72       | -0.78 | 0.44    |
|              | Menthol  | 3               | 0 - 2.7        | 0.65 $\pm$ 1.03       |       |         |
| Zn           | Original | 16              | 49.2 - 166.0   | 75.11 $\pm$ 27.62     | 0.35  | 0.73    |
|              | Menthol  | 8               | 56.8 - 80.7    | 71.60 $\pm$ 6.80      |       |         |

ND = Not detected

N/A = Not available

t = Independent t-test

U = Mann-Whitney U test

\*There is a significant difference when  $p < 0.05$

## 4.2 Correlation between heavy metals

Table 4.4 shows the correlation between two heavy metals. There were a moderate correlation between As-Pb ( $r=0.57$ ,  $p=0.004$ ), Cd-Pb ( $r=0.484$ ,  $p=0.016$ ), Cr-Mn ( $r=-0.491$ ,  $p=0.015$ ), Cr-Pb ( $r=-0.433$ ,  $p=0.034$ ), Cu-Hg ( $r=0.432$ ,  $p=0.035$ ), Mn-Ni ( $r=-0.575$ ,  $p=0.003$ ), Mn-Pb ( $r=0.414$ ,  $p=0.044$ ), and Ni-Pb ( $r=-0.579$ ,  $p=0.003$ ) (Table4.4). While there was a high correlation between Cr-Ni ( $r=0.845$ ,  $p=0.00$ ) (Table4.4). Other pair of heavy metals were not significantly correlated.

Table 4.4: Correlation between heavy metals

| Heavy metal | Unit    | As     | Cd    | Cr    | Cu    | Fe    | Hg    | Mn     | Ni     | Pb    | Zn |
|-------------|---------|--------|-------|-------|-------|-------|-------|--------|--------|-------|----|
| As          | r       |        |       |       |       |       |       |        |        |       |    |
|             | p-value |        |       |       |       |       |       |        |        |       |    |
| Cd          | r       | 0.24   |       |       |       |       |       |        |        |       |    |
|             | p-value | 0.25   |       |       |       |       |       |        |        |       |    |
| Cr          | r       | -0.19  | -0.36 |       |       |       |       |        |        |       |    |
|             | p-value | 0.35   | 0.08  |       |       |       |       |        |        |       |    |
| Cu          | r       | -0.10  | -0.34 | -0.03 |       |       |       |        |        |       |    |
|             | p-value | 0.61   | 0.10  | 0.88  |       |       |       |        |        |       |    |
| Fe          | r       | -0.02  | -0.12 | -0.09 | -0.01 |       |       |        |        |       |    |
|             | p-value | 0.92   | 0.56  | 0.66  | 0.95  |       |       |        |        |       |    |
| Hg          | r       | -0.13  | -0.07 | -0.20 | 0.43  | 0.07  |       |        |        |       |    |
|             | p-value | 0.53   | 0.71  | 0.34  | 0.03* | 0.74  |       |        |        |       |    |
| Mn          | r       | 0.34   | 0.25  | -0.49 | 0.01  | 0.12  | 0.32  |        |        |       |    |
|             | p-value | 0.09   | 0.23  | 0.01* | 0.95  | 0.55  | 0.12  |        |        |       |    |
| Ni          | r       | -0.28  | -0.36 | 0.84  | 0.17  | -0.01 | -0.26 | -0.57  |        |       |    |
|             | p-value | 0.18   | 0.08  | 0.00* | 0.41  | 0.97  | 0.21  | 0.003* |        |       |    |
| Pb          | r       | 0.57   | 0.48  | -0.43 | -0.34 | 0.13  | -0.28 | 0.41   | -0.57  |       |    |
|             | p-value | 0.004* | 0.01* | 0.03* | 0.09  | 0.54  | 0.18  | 0.04*  | 0.003* |       |    |
| Zn          | r       | 0.08   | -0.05 | -0.01 | 0.36  | -0.38 | -0.02 | 0.09   | 0.02   | -0.22 |    |
|             | p-value | 0.68   | 0.79  | 0.98  | 0.07  | 0.06  | 0.92  | 0.66   | 0.89   | 0.29  |    |

r = Pearson and Spearman correlation

\*There is a significant relationship when  $p < 0.05$

### 4.3 Determination of non-carcinogenic and carcinogenic health risk

Table 4.5 shows the non-carcinogenic health risk of heavy metals in the tobacco of commercial and DIY cigarette. There was no non-carcinogenic risk through ingestion and inhalation for all heavy metals measured. The HQ for all heavy metals were below than 1. For ingestion, the lowest non-carcinogenic risk was Pb (HQ= $9.15 \times 10^{-5}$ ) while the highest was Mn (HQ= $2.00 \times 10^{-3}$ ). For inhalation, the lowest non-carcinogenic risk was Mn (HQ= $8.40 \times 10^{-4}$ ) while the highest was Cd (HQ= $1.12 \times 10^{-1}$ ).

Table 4.6 shows the carcinogenic health risk of heavy metals in the tobacco of commercial and DIY cigarette. There was significant carcinogenic risk of developing 1 cancer cases per 1000000 populations for Cr (risk= $7.38 \times 10^{-6}$ ) and Ni (risk= $2.01 \times 10^{-6}$ ) through ingestion. Other heavy metals show no carcinogenic risk through ingestion and inhalation. For ingestion, the lowest carcinogenic risk was As (risk= $9.18 \times 10^{-9}$ ) while the highest was Ni (risk= $2.01 \times 10^{-6}$ ). For inhalation, the lowest carcinogenic risk was As (risk= $3.23 \times 10^{-11}$ ) while the highest was Cr (risk= $6.20 \times 10^{-7}$ ).

Cancer risks greater than  $1 \times 10^{-6}$  was considered unacceptable, and USEPA uses the general range of  $1 \times 10^{-4}$  to  $1 \times 10^{-6}$  as a 'target range' within which they aim to manage the risks.

Table 4.5: Non-carcinogenic risk

| Heavy metal | Mean (mg/kg) | Mean (mg/m <sup>3</sup> ) | Ingestion                      |                         | Inhalation                                  |                         |
|-------------|--------------|---------------------------|--------------------------------|-------------------------|---|-------------------------|
|             |              |                           | Average daily dose (mg/kg-day) | Hazard quotient (HQ)    | Average daily dose (mg/m <sup>3</sup> -day) | Hazard quotient (HQ)    |
| As          | 0.02         | 0.06135                   | 1.42 x 10 <sup>-8</sup>        | 4.76 x 10 <sup>-5</sup> | 1.75 x 10 <sup>-8</sup>                     | 1.16 x 10 <sup>-3</sup> |
| Cd          | 0.86         | 3.95                      | 6.14 x 10 <sup>-7</sup>        | 6.14 x 10 <sup>-4</sup> | 1.13 x 10 <sup>-6</sup>                     | 1.12 x 10 <sup>-1</sup> |
| Cr          | 28.37        | 60.34                     | 2.02 x 10 <sup>-5</sup>        | 1.35 x 10 <sup>-5</sup> | 1.72 x 10 <sup>-5</sup>                     | 5.74 x 10 <sup>-2</sup> |
| Cu          | 33.97        | 88.22                     | 2.42 x 10 <sup>-8</sup>        | 6.07 x 10 <sup>-4</sup> | 2.52 x 10 <sup>-5</sup>                     | N/A                     |
| Fe          | 1067.75      | 2436.83                   | 7.69 x 10 <sup>-4</sup>        | 1.09 x 10 <sup>-3</sup> | 6.96 x 10 <sup>-4</sup>                     | N/A                     |
| Hg          | 0.18         | 1.48                      | 1.28 x 10 <sup>-7</sup>        | 4.29 x 10 <sup>-4</sup> | 4.20 x 10 <sup>-7</sup>                     | 2.10 x 10 <sup>-3</sup> |
| Mn          | 393.04       | 882.14                    | 2.80 x 10 <sup>-4</sup>        | 2.00 x 10 <sup>-3</sup> | 2.52 x 10 <sup>-4</sup>                     | 8.40 x 10 <sup>-4</sup> |
| Ni          | 6.85         | 16.45                     | 4.89 x 10 <sup>-6</sup>        | 2.45 x 10 <sup>-4</sup> | 4.70 x 10 <sup>-6</sup>                     | 5.22 x 10 <sup>-2</sup> |
| Pb          | 0.46         | 3.9                       | 3.28 x 10 <sup>-7</sup>        | 9.15 x 10 <sup>-5</sup> | 1.11 x 10 <sup>-6</sup>                     | N/A                     |
| Zn          | 73.94        | 197.78                    | 5.28 x 10 <sup>-5</sup>        | 1.76 x 10 <sup>-4</sup> | 5.65 x 10 <sup>-5</sup>                     | N/A                     |

N/A = Not available

HQ > 1 indicates significant non-carcinogenic risk

HQ < 1 indicates no non-carcinogenic risk

Table 4.6: Carcinogenic risk

| Heavy metal | Mean (mg/kg) | Mean (mg/m <sup>3</sup> ) | Ingestion                               |                           | Inhalation   |                          |
|-------------|--------------|---------------------------|---|---------------------------|--|--------------------------|
|             |              |                           | Lifetime average daily dose (mg/kg-day) | Risk                      | Lifetime average daily dose (mg/m <sup>3</sup> -day) | Risk                     |
| As          | 0.02         | 0.06135                   | 6.12 x 10 <sup>-9</sup>                 | 9.18 x 10 <sup>-9</sup>   | 7.51 x 10 <sup>-9</sup>                              | 3.23 x 10 <sup>-11</sup> |
| Cd          | 0.86         | 3.95                      | 2.63 x 10 <sup>-7</sup>                 | 3.95 x 10 <sup>-7</sup>   | 4.83 x 10 <sup>-7</sup>                              | 8.70 x 10 <sup>-10</sup> |
| Cr          | 28.37        | 60.34                     | 8.68 x 10 <sup>-6</sup>                 | * 4.34 x 10 <sup>-6</sup> | 7.38 x 10 <sup>-6</sup>                              | 6.20 x 10 <sup>-7</sup>  |
| Ni          | 6.85         | 16.45                     | 2.09 x 10 <sup>-6</sup>                 | * 1.91 x 10 <sup>-6</sup> | 2.01 x 10 <sup>-6</sup>                              | 4.83 x 10 <sup>-10</sup> |

Risk < 1 x 10<sup>-6</sup> indicates no significant risk of developing cancer

Risk > 1 x 10<sup>-4</sup> indicates significant risk of developing 1 cancer cases per 10000 population

\*Risk > 1 x 10<sup>-6</sup> indicates significant risk of developing 1 cancer cases per 1000000 population

#### 4.4 Discussion on the comparison of heavy metals by types, prices and flavors

Based on the results, there were significant difference between heavy metal concentration with the types, prices and flavors of cigarette. Cr and Ni were found to be significantly different between types. Cu, Fe, Ni and Pb were found to be significantly different between prices. While Cr was found to be significantly different between flavors.

The difference in concentration of heavy metals detected may be affected by the use of chemical pesticide containing heavy metals. Previous study stated that metals enter the tobacco plant during growing by absorption from soil and from the application of fertilizers (Pappas, 2011). Other potential sources of heavy metals in finished cigarettes are pesticide and additives such as flavorings and humectants applied to products during the manufacturing process (Wertz, Kyriss, Paranjape, & Glantz, 2011).

A study on investigation of heavy metals in vegetable samples from the Obrenovac area stated that emission of coal combustion products from local thermal power plants is a possible source of heavy metals contamination in plant samples (Markovic, Cupac, DJurovic, Milinovic, & Kljajic, 2010).

Previous study have found that cigarettes made from tobacco grown in China have elevated levels of lead and cadmium compared to cigarettes made from tobacco grown elsewhere which is likely results from soil contamination due to environmental pollution (O'Connor et al., 2015).

Previous study found that the vital parts accumulating Cd, Pb in plant was the leaf and the sensitive parts were polluted by Cd, Pb while the subsidiary sensitive parts were polluted by Cr, Ni (Kim, Ziedonis, & Chen, 2007). Dried or process tobacco in the cigarette are made from the leaf part of tobacco. Heavy metals including Pb, Cr and Ni may accumulate in the tobacco leaf and being process into dried tobacco due to the impropriate use of pesticide (Marković et al., 2010). This factor may influence the concentration of heavy metals process in different type of cigarette.

Inappropriate use of pesticide, herbicides and insecticides such as metribuzin, trifluralin, pendimethalin, bifenthrin, chlorpyrifos, and cypermethrin as a plant protection products is considered to be the most probable reason of contamination (Markovic et al., 2010). Pesticide degradation is an important phenomenon that helps in remediating the contaminated soils. It is affected by a number of factors such as moisture content of soil, soil texture, and soil mineral contents (Shea, Machacek, & Comfort, 2004). These metals either are added to the soil along with pesticides or originate from the long-term application of wastewater and animal manures to agricultural soils (Khan, Cao, Zheng, Huang, & Zhu, 2008; Tariq, Shafiq, & Chotana, 2016).

#### 4.5 Discussion on the correlation between two heavy metals

Based on the results, there were correlation between heavy metals such as As-Pb, Cd-Pb, Cr-Mn, Cr-Pb, Cu-Hg, Mn-Ni, Mn-Pb, Ni-Pb and Cr-Ni (Table 4.4).

Heavy metals content in tobacco leaves is variable and depends on the conditions under which tobacco is grown and mostly on the composition and properties of the soils (Zaprjanova, Dospatliev, Angelova, & Ivanov, 2010). Based on previous study by Zaprjanova et al. (2010), there is a correlation the total content of Pb and Cd in the soil and their accumulation in tobacco cigarette.

Previous study reported a significant relationship between concentration of heavy metals in Oriental tobacco and concentration of heavy metal level in soils (Golia, Dimirkou, & Mitsios, 2007). The result is in line with the results of this study where there was a correlation between heavy metals.

A study have found statistically important relations between extracted zinc, manganese, nickel, and cadmium from the soil and their concentration in tobacco leaves (Adamu, Mulchi, & Bell, 1989; Pillai, 1998).

A study on heavy metals in an abandon barite mines shows significant correlation for heavy metals Hg-Fe, Mn-Ni, Mn-Pb and Pb-Zn. Comparing the results with this study Mn-Ni and Mn-Pb were found to have correlation while no correlation for Hg-Fe and Pb-Zn.

A study on plant biodiversity and heavy metals by Hernandez & Pastor, (2008) found a positive correlations between contents of Cd-Pb and Cr-Ni and Cu-Ni, but found negative correlation of Ni-Pb. Comparing the results with this study, Cd-Pb and Cr-Ni were also found to have a positive correlations, negative correlation detected for Ni-Pb while no correlation detected for Cu-Ni.

#### **4.6 Discussion on the determination of non-carcinogenic and carcinogenic health risk**

Health risk assessment (HRA) for non-carcinogenic were calculated using Average Daily Dose (ADD) and HQ. While HRA for carcinogenic were calculated using Lifetime Average Daily Dose (LADDi).

Based on the results of non-carcinogenic health risk for ingestion and inhalation, all heavy metals shows no significant risk ( $HQ < 1$ ). This is possibly because the concentration of heavy metals detected were too low which causes no significant risk.

Smoking cigarette can cause non-carcinogenic disease such as irritation of mucous membranes in humans, reduction in respiratory capacity in humans, blood problem, cardiovascular diseases (CVD), and kidney problem among humans on a long-term exposure to smoking (Behera et al., 2014). In addition, smoking contributes to development of atherosclerotic plaque and thrombosis (U.S. Department of Health and Human Services, 2010).

Smoking is a well-known risk factor for Chronic Obstructive Pulmonary Disorder (COPD), a group of lung diseases that includes emphysema and chronic bronchitis (Mannino, 2002). The primary cause of COPD in the developed world is tobacco smoke including secondhand and passive smokers (Mannino, 2002).

Smoking may affect the cardiovascular system which causes aortic aneurysm, coronary heart diseases, and other arterial diseases including cerebrovascular disease (Mazzone et al., 2010). Cigarette smoking also influences other cardiovascular risk factors, such as glucose intolerance and low serum levels of high-density lipoprotein cholesterol (HDL). Tobacco smoking can act as an independent risk factor for CVD, but it also has an interaction with other risk factors, such as high serum levels of lipids, hypertension and diabetes mellitus (U.S. Department of Health and Human Services, 2010).

Smoking can promote increased sympathetic activity, damage the endothelium, and accelerate atherosclerosis which are the risk factors for hypertension (Halperin, Gaziano, & Sesso, 2008). Tobacco smoking causes an estimated 12 % stroke mortality in low and middle income countries (Strong, Mathers, & Bonita, 2007). Stroke is also a major cause of long-term disability and has potentially enormous emotional and socioeconomic implications (Feigin, Lawes, Bennett, & Anderson, 2003).

Based on the result of carcinogenic health risk, there were heavy metals detected which may cause 1 cancer risk per 1000000 populations for Cr (risk= $7.38 \times 10^{-6}$ ) and Ni (risk= $2.01 \times 10^{-6}$ ) through ingestion. While no carcinogenic risk through inhalation. Significant carcinogenic risk of Cr and Ni maybe due to high level detected from the samples.

Literature study have reported that exposure to heavy metal compounds leads to disruptions in tumor suppressor gene expression, damage repair processes, and enzymatic activities concerned in metabolism via oxidative damage (Banfalvi, 2011). Recent studies found that there are increased risk of occupational diseases and cancer in workers from heavy metal-using industrial areas (Grimsrud & Andersen, 2012).

Cr is abundant in the earth's crust, and its toxicity depends on its chemical state (Barceloux, 1999). It exists in divalent to hexavalent compounds, but only the trivalent and hexavalent compounds have significant biological toxicity (Eastmond, Macgregor, & Slesinski, 2008). Cr compounds are usually found in industrial purposes such as chromite ore mining, pigment production, tanning of leather, formation of wood preservatives, and anticorrosive agents in cooking goods (Kotas & Stasicka, 2000). Lung cancer occurred more often in workers in the chromate-producing industry (Park et al., 2004). High concentrations of trivalent Cr can lead to cellular damage (Eastmond et al., 2008) while high levels of hexavalent Cr in the bloodstream can cause blood cell damage by oxidation and functional degradation of the liver and kidney (Dartsch, Hildenbrand, Kimmel, & Schmahl, 1998). Previous study found that diseases including lung cancer, skin allergy with dermatitis, and kidney diseases were induced by Cr and Cr compounds (Kim, Kim, & Seo, 2015).

Ni is widely used for industrial purposes because of its physicochemical properties. It is utilized in alloys and various products including rechargeable batteries, coins, electroplates, pigments, and stainless steel (IARC, 2007). People are often exposed to Ni by inhalation, direct skin contact, and oral consumption (Kasprzak, Sunderman, & Salnikow, 2003). Oral exposure to Ni also induces skin and oral epithelium damage (Trombetta et al., 2005). Breathing in Ni contaminated dust from Ni smelting, mining and tobacco smoking leads to significant damage to lungs and nasal cavities which causes diseases such as lung cancer and nasal cancer (Kupper et al., 2015). Several studies found that Ni exposure induces oxidative stress via a reduction in expression of antioxidant enzymes and DNA single and double-strand breaking (Kim et al., 2015). Previous study discovered that various toxicity in lung, nose, skin, kidney and liver were induced by Ni (Kim et al., 2015).

## CHAPTER 5

### CONCLUSION

In conclusion, As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, and Zn are heavy metals that were found in tobacco of commercial and DIY cigarette. The highest heavy metal concentration found both in commercial and DIY cigarette was Fe. There were some heavy metals concentration that was found significantly different by types (Cr and Ni), prices (Cu, Fe and Ni) and flavors (Cr). There was significant correlation between heavy metals (As-Pb, Cd-Pb, Cr-Mn, Cr-Pb, Cu-Hg, Mn-Ni, Mn-Pb, Ni-Pb, and Cr-Ni). There was no non-carcinogenic risk for inhalation and ingestion found. There was carcinogenic risk of developing 1 cancer cases per 1000000 populations for Cr and Ni through ingestion of tobacco.

## CHAPTER 6

### LIMITATION AND RECOMMENDATION

#### 6.1 Limitation of study

There were few limitations in this study. First and foremost, there were limited resources to select more brands, types, prices and flavors of commercial and DIY cigarette available in the market. Besides, this study uses the X-ray Fluorescent method which might have lower precision and detection limit than Inductively Coupled Plasma Mass Spectrometry (ICP-MS) method to detect heavy metal in tobacco of cigarette. This study does not gather primary data such as the socio-demographic of Malaysian population which is to be used in the determination of health risk. Lastly, this study does not take biological sample such as hair and saliva as biomarkers of heavy metals exposure in human.

## 6.2 Recommendation

There were few recommendations to counter the limitations of this study. First, this study recommends to conduct a research on more brands and flavors of cigarette available in the market. The other researcher may conduct the research using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) method to compare the concentration of heavy metals measured from X-Ray Fluorescence method. To further assess the exposure of heavy metals from tobacco to human, biomarkers such as saliva and hair samples can be taken and relate to the health risk. As this research focus more on the concentration of heavy metals in tobacco of cigarette, the other researcher may conduct a survey and questionnaire to assess the socio-demographic of Malaysian citizen. The information on Malaysian citizen can be used in the calculation of health risk and also explaining some parts of the research.

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APPENDIX

Sample A1

| Element | Concentration<br>/ppm | Uncertainty<br>/ppm | Area<br>Density<br>(μg/cm <sup>2</sup> ) | Counts   |
|---------|-----------------------|---------------------|--|----------|
| Ag 47   | ND <1.6               | ±1.6                |  | 0        |
| Al 13   | ND <21639             | ±21639              |  | 0        |
| As 33   | ND <0.1               | ±0.1                |  | 0        |
| Au 79   | ND <1.1               | ±1.1                |  | 0        |
| Ba 56   | 356                   | ±46.3               |  | 451.5    |
| Bi 83   | ND <0.6               | ±0.6                |  | 0        |
| Br 35   | 34.3                  | ±1.3                |  | 14380.2  |
| Cd 20   | 63270                 | ±396                |  | 71057.6  |
| Ce 48   | ND <2.0               | ±2.0                |  | 0        |
| Ce 58   | 40                    | ±21.6               |  | 91.8     |
| Cl 17   | 14890                 | ±756                |  | 2286.2   |
| Co 27   | ND <3.3               | ±3.3                |  | 0        |
| Cr 24   | 12.3                  | ±6.0                |  | 136.5    |
| Cu 29   | 52.6                  | ±2.4                |  | 7882.4   |
| Fe 26   | 879                   | ±19.5               |  | 18355.6  |
| Ga 31   | ND <0.2               | ±0.2                |  | 0        |
| Gd 62   | 0.6                   | ±0.1                |  | 97.3     |
| Hf 72   | 54                    | ±4.9                |  | 1535     |
| Hg 80   | 1                     | ±0.5                |  | 130.4    |
| In 49   | ND <1.8               | ±1.8                |  | 0        |
| K 19    | 62043                 | ±704                |  | 43425.7  |
| La 57   | ND <41.8              | ±41.8               |  | 0        |
| Mn 25   | 334                   | ±17.4               |  | 5732.6   |
| Mo 42   | 750                   | ±11.4               |  | 9.2      |
| Nd 60   | ND <17.7              | ±17.7               |  | 0        |
| Ni 28   | 4.1                   | ±0.7                |  | 222.8    |
| P 15    | ND <1.921             | ±1.921              |  | 0        |
| Pb 82   | ND <0.9               | ±0.9                |  | 0        |
| Pd 46   | ND <1.3               | ±1.3                |  | 0        |
| Pt 78   | ND <23.7              | ±23.7               |  | 0        |
| Rb 37   | 19.4                  | ±0.7                |  | 1488.1   |
| S 16    | ND <657               | ±657                |  | 0        |
| Sb 51   | ND <2.5               | ±2.5                |  | 0        |
| Se 34   | 1.1                   | ±0.3                |  | 36.1     |
| Si 14   | ND <3111              | ±3111               |  | 0        |
| Sn 50   | ND <2.5               | ±2.5                |  | 0        |
| Sr 38   | 389                   | ±1.7                |  | 153829.9 |
| Ta 73   | ND <7.4               | ±7.4                |  | 0        |
| Tl 20   | 59.7                  | ±30.9               |  | 108.1    |
| Tb 63   | 71.2                  | ±2.6                |  | 5762.2   |

APPENDIX

## Sample A1

| Element | Concentration<br>/ppm | Uncertainty<br>/ppm | Area<br>Density<br>(ug/cm <sup>2</sup> ) | Counts   |
|---------|-----------------------|---------------------|--|----------|
| Ag 47   | ND <1.6               | ± 1.6               | -  | 0        |
| Al 13   | ND <21639             | ± 21639             | -  | 0        |
| As 33   | ND <0.3               | ± 0.3               | -  | 0        |
| Au 79   | ND <1.1               | ± 1.1               | -  | 0        |
| Ba 56   | 356                   | ± 68.2              | -  | 453.9    |
| Bi 83   | ND <0.6               | ± 0.6               | -  | 0        |
| Br 35   | 44.9                  | ± 1.2               | -  | 14350.2  |
| Ca 20   | 63270                 | ± 566               | -  | 71067.6  |
| Cd 48   | ND <2.0               | ± 2.0               | -  | 0        |
| Ce 58   | 40                    | ± 21.6              | -  | 91.8     |
| Cl 17   | 13990                 | ± 755               | -  | 2206.2   |
| Co 27   | ND <3.8               | ± 3.8               | -  | 0        |
| Cr 24   | 12.1                  | ± 6.0               | -  | 130.5    |
| Cu 29   | 52.5                  | ± 2.4               | -  | 3568.4   |
| Fe 26   | 879                   | ± 19.6              | -  | 18195.6  |
| Ga 31   | ND <0.7               | ± 0.7               | -  | 0        |
| Ge 32   | 0.6                   | ± 0.5               | -  | 97.9     |
| Hf 72   | 54                    | ± 4.9               | -  | 1591     |
| Hg 80   | 1                     | ± 0.5               | -  | 110.4    |
| In 49   | ND <2.4               | ± 2.4               | -  | 0        |
| K 19    | 62944                 | ± 703               | -  | 43325.7  |
| La 57   | ND <43.4              | ± 43.4              | -  | 0        |
| Mn 25   | 434                   | ± 17.3              | -  | 5732.6   |
| Mo 42   | 259                   | ± 11.4              | -  | 9.2      |
| Nd 60   | ND <17.7              | ± 17.7              | -  | 0        |
| Ni 28   | 4.1                   | ± 0.7               | -  | 222.8    |
| P 15    | ND <1391              | ± 1391              | -  | 0        |
| Pb 82   | ND <0.9               | ± 0.9               | -  | 0        |
| Pd 46   | ND <1.5               | ± 1.5               | -  | 0        |
| Pr 59   | ND <21.7              | ± 21.7              | -  | 0        |
| Rb 37   | 16.4                  | ± 0.7               | -  | 7446.1   |
| S 16    | ND <657               | ± 657               | -  | 0        |
| Sb 51   | ND <2.5               | ± 2.5               | -  | 0        |
| Se 34   | 1.1                   | ± 0.4               | -  | 283      |
| Si 14   | ND <2111              | ± 2111              | -  | 0        |
| Sn 50   | ND <2.5               | ± 2.5               | -  | 0        |
| Sr 38   | 289                   | ± 2.2               | -  | 151029.9 |
| Ta 73   | ND <2.4               | ± 2.4               | -  | 0        |
| Ti 22   | 59.7                  | ± 30.9              | -  | 169.1    |
| Zn 30   | 71.2                  | ± 2.6               | -  | 6762.2   |

## Sample A2

| Element | Concentration<br>/ppm | Uncertainty<br>/ppm | Area<br>Density<br>(ug/cm <sup>2</sup> ) | Counts   |
|---------|-----------------------|---------------------|--|----------|
| Ag 47   | ND <2.1               | ± 2.1               | -  | 0        |
| Al 13   | ND <22094             | ± 22094             | -  | 0        |
| As 33   | ND <0.2               | ± 0.2               | -  | 0        |
| Au 79   | ND <0.9               | ± 0.9               | -  | 0        |
| Ba 56   | 375                   | ± 53.8              | -  | 599.8    |
| Bi 83   | ND <0.5               | ± 0.5               | -  | 0        |
| Br 35   | 83.3                  | ± 1.5               | -  | 33187.3  |
| Ca 20   | 71386                 | ± 606               | -  | 102516   |
| Cd 48   | ND <2.4               | ± 2.4               | -  | 0        |
| Ce 58   | ND <25.8              | ± 25.8              | -  | 0        |
| Cl 17   | 13921                 | ± 753               | -  | 2879.7   |
| Co 27   | ND <3.5               | ± 3.5               | -  | 0        |
| Cr 24   | 18.2                  | ± 6.6               | -  | 245.6    |
| Cu 29   | 43.9                  | ± 2.0               | -  | 3729     |
| Fe 26   | 1039                  | ± 18.9              | -  | 26889.8  |
| Ga 31   | ND <0.6               | ± 0.6               | -  | 0        |
| Ge 32   | 0.8                   | ± 0.4               | -  | 152.8    |
| Hf 72   | 40.3                  | ± 3.9               | -  | 1481.4   |
| Hg 80   | ND <0.6               | ± 0.6               | -  | 55.3     |
| In 49   | ND <1.8               | ± 1.8               | -  | 0        |
| K 19    | 72617                 | ± 753               | -  | 65529.7  |
| La 57   | ND <39.6              | ± 39.6              | -  | 0        |
| Mn 25   | 281                   | ± 12.7              | -  | 4646.4   |
| Mo 42   | 350                   | ± 13.5              | -  | 16.2     |
| Nd 60   | ND <15.7              | ± 15.7              | -  | 0        |
| Ni 28   | 7.2                   | ± 1.0               | -  | 494      |
| P 15    | ND <1467              | ± 1467              | -  | 0        |
| Pb 82   | ND <0.8               | ± 0.8               | -  | 0        |
| Pd 46   | 3.4                   | ± 1.9               | -  | 0.6      |
| Pr 59   | ND <19.6              | ± 19.6              | -  | 0        |
| Rb 37   | 18.7                  | ± 0.7               | -  | 10538.8  |
| S 16    | ND <721               | ± 721               | -  | 0        |
| Sb 51   | ND <3.1               | ± 3.1               | -  | 0        |
| Se 34   | ND <0.3               | ± 0.3               | -  | 0        |
| Si 14   | ND <2282              | ± 2282              | -  | 0        |
| Sn 50   | ND <3.0               | ± 3.0               | -  | 0        |
| Sr 38   | 251                   | ± 1.8               | -  | 163732.6 |
| Ta 73   | ND <2.0               | ± 2.0               | -  | 0        |
| Ti 22   | 296                   | ± 35.1              | -  | 1052     |
| Zn 30   | 70.7                  | ± 2.3               | -  | 8380.3   |

## Sample B1

| Element | Concentration<br>/ppm | Uncertainty<br>/ppm | Area<br>Density<br>(ug/cm <sup>2</sup> ) | Counts   |
|---------|-----------------------|---------------------|--|----------|
| Ag 47   | ND <1.7               | ± 1.7               | -  | 0        |
| Al 13   | ND <21830             | ± 21830             | -  | 0        |
| As 33   | ND <0.3               | ± 0.3               | -  | 0        |
| Au 79   | ND <0.9               | ± 0.9               | -  | 0        |
| Ba 56   | ND <215               | ± 215               | -  | 0        |
| Bi 83   | ND <0.6               | ± 0.6               | -  | 0        |
| Br 35   | 74.3                  | ± 1.5               | -  | 23493.2  |
| Ca 20   | 64563                 | ± 571               | -  | 72114.4  |
| Cd 48   | ND <2.0               | ± 2.0               | -  | 0        |
| Ce 58   | 99.2                  | ± 20.4              | -  | 226      |
| Cl 17   | 12951                 | ± 729               | -  | 2032.5   |
| Co 27   | ND <4.6               | ± 4.6               | -  | 0        |
| Cr 24   | 21.4                  | ± 6.7               | -  | 228      |
| Cu 29   | 50                    | ± 2.4               | -  | 3361.5   |
| Fe 26   | 1556                  | ± 25.9              | -  | 31927.5  |
| Ga 31   | ND <0.7               | ± 0.7               | -  | 0        |
| Ge 32   | ND <0.5               | ± 0.5               | -  | 0        |
| Hf 72   | 50.1                  | ± 4.8               | -  | 1457.6   |
| Hg 80   | ND <0.4               | ± 0.4               | -  | 0        |
| In 49   | ND <1.5               | ± 1.5               | -  | 0        |
| K 19    | 63990                 | ± 708               | -  | 43929.9  |
| La 57   | ND <45.5              | ± 45.5              | -  | 0        |
| Mn 25   | 350                   | ± 15.7              | -  | 4590.8   |
| Mo 42   | 262                   | ± 11.5              | -  | 9.2      |
| Nd 60   | ND <18.2              | ± 18.2              | -  | 0        |
| Ni 28   | 7.2                   | ± 1.0               | -  | 389      |
| P 15    | ND <1400              | ± 1400              | -  | 0        |
| Pb 82   | ND <0.9               | ± 0.9               | -  | 0        |
| Pd 46   | ND <1.4               | ± 1.4               | -  | 0        |
| Pr 59   | ND <21.5              | ± 21.5              | -  | 0        |
| Rb 37   | 17.5                  | ± 0.7               | -  | 7849.9   |
| S 16    | ND <677               | ± 677               | -  | 0        |
| Sb 51   | ND <2.5               | ± 2.5               | -  | 0        |
| Se 34   | ND <0.3               | ± 0.3               | -  | 0        |
| Si 14   | ND <2064              | ± 2064              | -  | 0        |
| Sn 50   | ND <2.4               | ± 2.4               | -  | 0        |
| Sr 38   | 256                   | ± 2.1               | -  | 132247.9 |
| Ta 73   | ND <2.4               | ± 2.4               | -  | 0        |
| Ti 22   | 229                   | ± 27.3              | -  | 642.7    |
| Zn 30   | 77.4                  | ± 2.7               | -  | 7269.5   |

## Sample B2

| Element | Concentration<br>/ppm | Uncertainty<br>/ppm | Area<br>Density<br>(ug/cm <sup>2</sup> ) | Counts   |
|---------|-----------------------|---------------------|--|----------|
| Ag 47   | ND <1.8               | ± 1.8               | -  | 0        |
| Al 13   | ND <20623             | ± 20623             | -  | 0        |
| As 33   | ND <0.3               | ± 0.3               | -  | 0        |
| Au 79   | ND <0.9               | ± 0.9               | -  | 0        |
| Ba 56   | 358                   | ± 50.3              | -  | 435.9    |
| Bi 83   | ND <0.6               | ± 0.6               | -  | 0        |
| Br 35   | 78.1                  | ± 1.6               | -  | 23910.9  |
| Ca 20   | 60394                 | ± 549               | -  | 64437.1  |
| Cd 48   | 2.2                   | ± 2.1               | -  | 0.5      |
| Ce 58   | ND <30.5              | ± 30.5              | -  | 0        |
| Cl 17   | 10463                 | ± 662               | -  | 1535     |
| Co 27   | ND <4.5               | ± 4.5               | -  | 0        |
| Cr 24   | 17.5                  | ± 6.2               | -  | 180.3    |
| Cu 29   | 45.6                  | ± 2.3               | -  | 2960.9   |
| Fe 26   | 1391                  | ± 25.0              | -  | 27553.4  |
| Ga 31   | ND <0.7               | ± 0.7               | -  | 0        |
| Ge 32   | 0.8                   | ± 0.5               | -  | 122.1    |
| Hf 72   | 56.3                  | ± 5.0               | -  | 1585.4   |
| Hg 80   | 1.5                   | ± 0.6               | -  | 168.7    |
| In 49   | ND <2.3               | ± 2.3               | -  | 0        |
| K 19    | 57701                 | ± 673               | -  | 37240.9  |
| La 57   | ND <45.1              | ± 45.1              | -  | 0        |
| Mn 25   | 352                   | ± 16.1              | -  | 4452.4   |
| Mo 42   | 264                   | ± 11.5              | -  | 8.7      |
| Nd 60   | ND <18.6              | ± 18.6              | -  | 0        |
| Ni 28   | 6.5                   | ± 1.0               | -  | 340.1    |
| P 15    | ND <1338              | ± 1338              | -  | 0        |
| Pb 82   | ND <0.9               | ± 0.9               | -  | 0        |
| Pd 46   | ND <1.4               | ± 1.4               | -  | 0        |
| Pr 59   | ND <22.5              | ± 22.5              | -  | 0        |
| Rb 37   | 16.6                  | ± 0.7               | -  | 7204.1   |
| S 16    | ND <674               | ± 674               | -  | 0        |
| Sb 51   | ND <2.5               | ± 2.5               | -  | 0        |
| Se 34   | 0.9                   | ± 0.4               | -  | 217.8    |
| Si 14   | ND <2113              | ± 2113              | -  | 0        |
| Sn 50   | ND <3.9               | ± 3.9               | -  | 0        |
| Sr 38   | 248                   | ± 2.1               | -  | 124237.7 |
| Ta 73   | ND <2.4               | ± 2.4               | -  | 0        |
| Zn 30   | 70.8                  | ± 2.6               | -  | 6429.2   |

## Sample C1

| Element | Concentration<br>/ppm | Uncertainty<br>/ppm | Area<br>Density<br>(ug/cm <sup>2</sup> ) | Counts   |
|---------|-----------------------|---------------------|--|----------|
| Ag 47   | ND <2.3               | ± 2.3               | -  | 0        |
| Al 13   | ND <22230             | ± 22230             | -  | 0        |
| As 33   | ND <0.2               | ± 0.2               | -  | 0        |
| Au 79   | ND <0.7               | ± 0.7               | -  | 0        |
| Ba 56   | 436                   | ± 62.1              | -  | 778      |
| Bi 83   | ND <0.5               | ± 0.5               | -  | 0        |
| Br 35   | 41.3                  | ± 1.0               | -  | 18356.1  |
| Ca 20   | 71938                 | ± 613               | -  | 115364.9 |
| Cd 48   | ND <2.8               | ± 2.8               | -  | 0        |
| Ce 58   | ND <23.2              | ± 23.2              | -  | 0        |
| Cl 17   | 15346                 | ± 787               | -  | 3587.9   |
| Co 27   | ND <3.4               | ± 3.4               | -  | 0        |
| Cr 24   | 50.9                  | ± 8.7               | -  | 765.1    |
| Cu 29   | 29.1                  | ± 1.5               | -  | 2754.2   |
| Fe 26   | 1076                  | ± 18.2              | -  | 31090.1  |
| Ga 31   | ND <0.5               | ± 0.5               | -  | 0        |
| Ge 32   | ND <0.3               | ± 0.3               | -  | 0        |
| Hf 72   | 36.6                  | ± 3.4               | -  | 1502.1   |
| Hg 80   | ND <0.6               | ± 0.6               | -  | 0        |
| In 49   | ND <2.2               | ± 2.2               | -  | 0        |
| K 19    | 76477                 | ± 774               | -  | 77714.3  |
| La 57   | ND <36.9              | ± 36.9              | -  | 0        |
| Mn 25   | 339                   | ± 13.1              | -  | 6255.4   |
| Mo 42   | 482                   | ± 15.9              | -  | 25.6     |
| Nd 60   | ND <13.9              | ± 13.9              | -  | 0        |
| Ni 28   | 9                     | ± 1.1               | -  | 690.8    |
| P 15    | ND <2122              | ± 2122              | -  | 0        |
| Pb 82   | ND <0.7               | ± 0.7               | -  | 0        |
| Pd 46   | ND <2.0               | ± 2.0               | -  | 0        |
| Pr 59   | ND <18.8              | ± 18.8              | -  | 0        |
| Rb 37   | 26.8                  | ± 0.7               | -  | 16880.2  |
| Rh 45   | 4.5                   | ± 2.3               | -  | 0.7      |
| S 16    | 5798                  | ± 861               | -  | 574.5    |
| Sb 51   | ND <3.6               | ± 3.6               | -  | 0        |
| Se 34   | ND <0.3               | ± 0.3               | -  | 0        |
| Si 14   | ND <3432              | ± 3432              | -  | 0        |
| Sn 50   | ND <3.7               | ± 3.7               | -  | 0        |
| Sr 38   | 135                   | ± 1.3               | -  | 98446.8  |
| Ta 73   | ND <1.8               | ± 1.8               | -  | 0        |
| Ti 22   | 187                   | ± 31.1              | -  | 741.6    |
| Zn 30   | 64                    | ± 2.1               | -  | 8458.6   |

## Sample C2

| Element | Concentration<br>/ppm | Uncertainty<br>/ppm | Area<br>Density<br>(ug/cm <sup>2</sup> ) | Counts  |
|---------|-----------------------|---------------------|--|---------|
| Ag 47   | ND <1.8               | ± 1.8               | -  | 0       |
| Al 13   | ND <21302             | ± 21302             | -  | 0       |
| As 33   | ND <0.3               | ± 0.3               | -  | 0       |
| Au 79   | ND <1.1               | ± 1.1               | -  | 0       |
| Ba 56   | 314                   | ± 79.9              | -  | 395.1   |
| Bi 83   | ND <0.6               | ± 0.6               | -  | 0       |
| Br 35   | 48                    | ± 1.3               | -  | 15074.1 |
| Ca 20   | 64149                 | ± 569               | -  | 71411.7 |
| Cd 48   | ND <1.9               | ± 1.9               | -  | 0       |
| Ce 58   | 158                   | ± 23.9              | -  | 357.9   |
| Cl 17   | 10471                 | ± 663               | -  | 1629.4  |
| Co 27   | ND <4.6               | ± 4.6               | -  | 0       |
| Cr 24   | 19                    | ± 6.8               | -  | 202     |
| Cu 29   | 46.1                  | ± 2.2               | -  | 3081.8  |
| Fe 26   | 1581                  | ± 26.2              | -  | 32303.6 |
| Ga 31   | ND <0.7               | ± 0.7               | -  | 0       |
| Ge 32   | 0.6                   | ± 0.5               | -  | 85.2    |
| Hf 72   | 50.3                  | ± 4.7               | -  | 1456.3  |
| Hg 80   | 0.8                   | ± 0.5               | -  | 91.7    |
| In 49   | ND <1.4               | ± 1.4               | -  | 0       |
| K 19    | 63955                 | ± 707               | -  | 43773.3 |
| La 57   | ND <46.5              | ± 46.5              | -  | 0       |
| Mn 25   | 566                   | ± 19.8              | -  | 7381.6  |
| Mo 42   | 239                   | ± 11.0              | -  | 8.3     |
| Nd 60   | ND <17.4              | ± 17.4              | -  | 0       |
| Ni 28   | 6.2                   | ± 0.9               | -  | 336.3   |
| P 15    | ND <1389              | ± 1389              | -  | 0       |
| Pb 82   | ND <0.9               | ± 0.9               | -  | 0       |
| Pd 46   | ND <1.4               | ± 1.4               | -  | 0       |
| Pr 59   | ND <22.2              | ± 22.2              | -  | 0       |
| Rb 37   | 28.4                  | ± 0.8               | -  | 12680.1 |
| S 16    | ND <712               | ± 712               | -  | 0       |
| Sb 51   | ND <2.5               | ± 2.5               | -  | 0       |
| Se 34   | ND <0.3               | ± 0.3               | -  | 0       |
| Si 14   | ND <2157              | ± 2157              | -  | 0       |
| Sn 50   | ND <2.4               | ± 2.4               | -  | 0       |
| Sr 38   | 167                   | ± 1.7               | -  | 85881.2 |
| Ta 73   | ND <2.4               | ± 2.4               | -  | 0       |
| Ti 22   | 314                   | ± 31.0              | -  | 879.7   |
| Zn 30   | 80.7                  | ± 2.8               | -  | 7539.8  |

## Sample D1

| Element | Concentration<br>/ppm | Uncertainty<br>/ppm | Area<br>Density<br>(ug/cm <sup>2</sup> ) | Counts   |
|---------|-----------------------|---------------------|--|----------|
| Ag 47   | ND <2.2               | ± 2.2               | -  | 0        |
| Al 13   | ND <21913             | ± 21913             | -  | 0        |
| As 33   | ND <0.2               | ± 0.2               | -  | 0        |
| Au 79   | ND <0.7               | ± 0.7               | -  | 0        |
| Ba 56   | 426                   | ± 57.5              | -  | 718.4    |
| Bi 83   | ND <0.5               | ± 0.5               | -  | 0        |
| Br 35   | 30.1                  | ± 0.9               | -  | 12589.5  |
| Ca 20   | 81738                 | ± 648               | -  | 126779.8 |
| Cd 48   | ND <2.7               | ± 2.7               | -  | 0        |
| Ce 58   | ND <24.8              | ± 24.8              | -  | 0        |
| Cl 17   | 13347                 | ± 740               | -  | 2981.1   |
| Co 27   | ND <3.3               | ± 3.3               | -  | 0        |
| Cr 24   | 38                    | ± 7.9               | -  | 538.8    |
| Cu 29   | 40.6                  | ± 1.9               | -  | 3627.2   |
| Fe 26   | 948                   | ± 17.6              | -  | 25801.2  |
| Ga 31   | ND <0.6               | ± 0.6               | -  | 0        |
| Ge 32   | ND <0.3               | ± 0.3               | -  | 0        |
| Hf 72   | 36.2                  | ± 3.7               | -  | 1400.6   |
| Hg 80   | ND <0.4               | ± 0.4               | -  | 0        |
| In 49   | ND <3.2               | ± 3.2               | -  | 0        |
| K 19    | 72630                 | ± 754               | -  | 70807.8  |
| La 57   | ND <38.0              | ± 38.0              | -  | 0        |
| Mn 25   | 314                   | ± 13.0              | -  | 5464.3   |
| Mo 42   | 460                   | ± 15.7              | -  | 23.4     |
| Nd 60   | ND <15.0              | ± 15.0              | -  | 0        |
| Ni 28   | 9.5                   | ± 1.1               | -  | 682.8    |
| P 15    | ND <2264              | ± 2264              | -  | 0        |
| Pb 82   | ND <0.8               | ± 0.8               | -  | 0        |
| Pd 46   | 3.3                   | ± 2.0               | -  | 0.6      |
| Pr 59   | ND <19.5              | ± 19.5              | -  | 0        |
| Rb 37   | 24.2                  | ± 0.7               | -  | 14357.4  |
| Rh 45   | 4                     | ± 2.3               | -  | 0.6      |
| S 16    | 6422                  | ± 895               | -  | 608.7    |
| Sb 51   | ND <3.5               | ± 3.5               | -  | 0        |
| Se 34   | 0.5                   | ± 0.3               | -  | 170.5    |
| Si 14   | ND <3263              | ± 3263              | -  | 0        |
| Sn 50   | ND <3.5               | ± 3.5               | -  | 0        |
| Sr 38   | 195                   | ± 1.6               | -  | 133665.9 |
| Ta 73   | ND <2.0               | ± 2.0               | -  | 0        |
| Ti 22   | 123                   | ± 27.9              | -  | 459      |
| Zn 30   | 72.8                  | ± 2.3               | -  | 9061.8   |

## Sample D2

| Element | Concentration /ppm | Uncertainty /ppm | Area Density (ug/cm <sup>2</sup> ) | Counts   |
|---------|--------------------|------------------|------------------------------------|----------|
| Ag 47   | ND <2.3            | ± 2.3            | -                                  | 0        |
| Al 13   | ND <21915          | ± 21915          | -                                  | 0        |
| As 33   | ND <0.2            | ± 0.2            | -                                  | 0        |
| Au 79   | ND <0.7            | ± 0.7            | -                                  | 0        |
| Ba 56   | 335                | ± 52.8           | -                                  | 556.8    |
| Bi 83   | ND <0.5            | ± 0.5            | -                                  | 0        |
| Br 35   | 29                 | ± 0.9            | -                                  | 12004.5  |
| Ca 20   | 82067              | ± 646            | -                                  | 125819.2 |
| Cd 48   | ND <2.7            | ± 2.7            | -                                  | 0.8      |
| Ce 58   | ND <115            | ± 115            | -                                  | 0        |
| Cl 17   | 14160              | ± 760            | -                                  | 3085.8   |
| Co 27   | ND <3.3            | ± 3.3            | -                                  | 0        |
| Cr 24   | 29.3               | ± 7.3            | -                                  | 410.7    |
| Cu 29   | 42.6               | ± 1.9            | -                                  | 3753.8   |
| Fe 26   | 958                | ± 17.8           | -                                  | 25761.5  |
| Ga 31   | ND <0.6            | ± 0.6            | -                                  | 0        |
| Ge 32   | ND <0.4            | ± 0.4            | -                                  | 0        |
| Hf 72   | 37.7               | ± 3.8            | -                                  | 1438.8   |
| Hg 80   | ND <0.6            | ± 0.6            | -                                  | 0        |
| In 49   | ND <2.0            | ± 2.0            | -                                  | 0        |
| K 19    | 66826              | ± 724            | -                                  | 63462.6  |
| La 57   | ND <38.3           | ± 38.3           | -                                  | 0        |
| Mn 25   | 278                | ± 12.4           | -                                  | 4771.7   |
| Mo 42   | 457                | ± 15.5           | -                                  | 22.6     |
| Nd 60   | ND <14.7           | ± 14.7           | -                                  | 0        |
| Ni 28   | 8                  | ± 1.0            | -                                  | 571.7    |
| P 15    | ND <2239           | ± 2239           | -                                  | 0        |
| Pb 82   | ND <0.8            | ± 0.8            | -                                  | 0        |
| Pd 46   | 3.6                | ± 2.0            | -                                  | 0.7      |
| Pr 59   | ND <19.5           | ± 19.5           | -                                  | 0        |
| Rb 37   | 21.9               | ± 0.6            | -                                  | 12857    |
| S 16    | 6117               | ± 884            | -                                  | 565.4    |
| Sb 51   | ND <3.4            | ± 3.4            | -                                  | 0        |
| Se 34   | ND <0.3            | ± 0.3            | -                                  | 0        |
| Si 14   | ND <2245           | ± 2245           | -                                  | 0        |
| Sn 50   | ND <3.4            | ± 3.4            | -                                  | 0        |
| Sr 38   | 196                | ± 1.6            | -                                  | 132431   |
| Ta 73   | ND <2.0            | ± 2.0            | -                                  | 0        |
| Ti 22   | 106                | ± 26.3           | -                                  | 390.7    |
| Zn 30   | 75.2               | ± 2.3            | -                                  | 9259     |

# Sample E1

| Element | Concentration /ppm | Uncertainty /ppm | Area Density (ug/cm <sup>2</sup> ) | Counts   |
|---------|--------------------|------------------|------------------------------------|----------|
| Ag 47   | ND <2.2            | ± 2.2            | -                                  | 0        |
| Al 13   | ND <20933          | ± 20933          | -                                  | 0        |
| As 33   | ND <0.3            | ± 0.3            | -                                  | 0        |
| Au 79   | ND <0.8            | ± 0.8            | -                                  | 0        |
| Ba 56   | 492                | ± 66.1           | -                                  | 858.3    |
| Bi 83   | ND <0.5            | ± 0.5            | -                                  | 0        |
| Br 35   | 186                | ± 2.1            | -                                  | 80507.8  |
| Ca 20   | 90783              | ± 677            | -                                  | 149337.2 |
| Cd 48   | ND <2.8            | ± 2.8            | -                                  | 0.9      |
| Ce 58   | ND <23.9           | ± 23.9           | -                                  | 0        |
| Cl 17   | 18372              | ± 858            | -                                  | 4295.2   |
| Co 27   | ND <3.5            | ± 3.5            | -                                  | 0        |
| Cr 24   | 18.1               | ± 6.7            | -                                  | 265.9    |
| Cu 29   | 29.3               | ± 1.5            | -                                  | 2700.7   |
| Fe 26   | 1165               | ± 19.2           | -                                  | 32828    |
| Ga 31   | ND <0.6            | ± 0.6            | -                                  | 0        |
| Ge 32   | ND <0.3            | ± 0.3            | -                                  | 0        |
| Hf 72   | 33.6               | ± 3.4            | -                                  | 1341.3   |
| Hg 80   | ND <0.4            | ± 0.4            | -                                  | 0        |
| In 49   | ND <3.4            | ± 3.4            | -                                  | 0        |
| K 19    | 62913              | ± 706            | -                                  | 63487.3  |
| La 57   | ND <37.5           | ± 37.5           | -                                  | 0        |
| Mn 25   | 411                | ± 14.4           | -                                  | 7407.6   |
| Mo 42   | 488                | ± 16.2           | -                                  | 25.9     |
| Nd 60   | ND <14.4           | ± 14.4           | -                                  | 0        |
| Ni 28   | 5                  | ± 0.8            | -                                  | 375.5    |
| P 15    | ND <2322           | ± 2322           | -                                  | 0        |
| Pb 82   | 1.2                | ± 0.3            | -                                  | 293.9    |
| Pd 46   | 3.5                | ± 2.0            | -                                  | 0.7      |
| Pr 59   | ND <18.6           | ± 18.6           | -                                  | 0        |
| Rb 37   | 17.1               | ± 0.7            | -                                  | 10477.4  |
| S 16    | 6341               | ± 908            | -                                  | 629.1    |
| Sb 51   | ND <3.5            | ± 3.5            | -                                  | 0        |
| Se 34   | ND <0.3            | ± 0.3            | -                                  | 0        |
| Si 14   | ND <3335           | ± 3335           | -                                  | 0        |
| Sn 50   | ND <3.5            | ± 3.5            | -                                  | 0        |
| Sr 38   | 149                | ± 1.4            | -                                  | 105220.6 |
| Ta 73   | ND <1.9            | ± 1.9            | -                                  | 0        |
| Ti 22   | 208                | ± 32.9           | -                                  | 805.3    |
| Zn 30   | 60.9               | ± 2.1            | -                                  | 7832.8   |

## Sample E2

| Element | Concentration<br>/ppm | Uncertainty<br>/ppm | Area<br>Density<br>(ug/cm <sup>2</sup> ) | Counts  |
|---------|-----------------------|---------------------|--|---------|
| Ag 47   | ND <2.0               | ± 2.0               | -  | 0       |
| Al 13   | ND <19402             | ± 19402             | -  | 0       |
| As 33   | 0.2                   | ± 0.1               | -  | 53.3    |
| Au 79   | ND <0.7               | ± 0.7               | -  | 0       |
| Ba 56   | ND <37.3              | ± 37.3              | -  | 3.8     |
| Bi 83   | ND <0.5               | ± 0.5               | -  | 0       |
| Br 35   | 30.8                  | ± 0.9               | -  | 12832.6 |
| Ca 20   | 57957                 | ± 535               | -  | 83124.9 |
| Cd 48   | 5                     | ± 2.7               | -  | 1.5     |
| Ce 58   | 36.4                  | ± 16.7              | -  | 108     |
| Cl 17   | 11446                 | ± 691               | -  | 2225.8  |
| Co 27   | ND <3.4               | ± 3.4               | -  | 0       |
| Cr 24   | 15.1                  | ± 5.9               | -  | 210.1   |
| Cu 29   | 30.3                  | ± 1.6               | -  | 2671.4  |
| Fe 26   | 994                   | ± 18.2              | -  | 26673.6 |
| Ga 31   | ND <0.6               | ± 0.6               | -  | 0       |
| Ge 32   | ND <0.4               | ± 0.4               | -  | 0       |
| Hf 72   | 38.1                  | ± 3.6               | -  | 1458.1  |
| Hg 80   | ND <0.4               | ± 0.4               | -  | 0       |
| In 49   | ND <1.8               | ± 1.8               | -  | 0       |
| K 19    | 51538                 | ± 638               | -  | 44004.8 |
| La 57   | ND <37.4              | ± 37.4              | -  | 0       |
| Mn 25   | 452                   | ± 15.5              | -  | 7745    |
| Mo 42   | 362                   | ± 13.3              | -  | 15.8    |
| Nd 60   | ND <14.6              | ± 14.6              | -  | 0       |
| Ni 28   | 4.9                   | ± 0.8               | -  | 351.5   |
| P 15    | ND <1946              | ± 1946              | -  | 0       |
| Pb 82   | 2.7                   | ± 0.3               | -  | 665.6   |
| Pd 46   | ND <1.7               | ± 1.7               | -  | 0       |
| Pr 59   | ND <13.2              | ± 13.2              | -  | 0       |
| Rb 37   | 19.4                  | ± 0.6               | -  | 11425.9 |
| Rh 45   | 4.1                   | ± 2.0               | -  | 0.5     |
| S 16    | ND <727               | ± 727               | -  | 0       |
| Sb 51   | ND <3.1               | ± 3.1               | -  | 0       |
| Se 34   | ND <0.3               | ± 0.3               | -  | 0       |
| Si 14   | ND <2080              | ± 2080              | -  | 0       |
| Sn 50   | ND <2.9               | ± 2.9               | -  | 0       |
| Sr 38   | 85.1                  | ± 1.1               | -  | 58002   |
| Ta 73   | ND <2.0               | ± 2.0               | -  | 0       |
| Ti 22   | 298                   | ± 29.5              | -  | 1087.9  |
| Zn 30   | 74.2                  | ± 2.3               | -  | 9152.6  |

# Sample F1

| Element | Concentration<br>/ppm | Uncertainty<br>/ppm | Area<br>Density<br>(ug/cm <sup>2</sup> ) | Counts   |
|---------|-----------------------|---------------------|--|----------|
| Ag 47   | ND <2.2               | ± 2.2               | -  | 0        |
| Al 13   | ND <21883             | ± 21883             | -  | 0        |
| As 33   | ND <0.1               | ± 0.1               | -  | 28.6     |
| Au 79   | ND <0.8               | ± 0.8               | -  | 0        |
| Ba 56   | 395                   | ± 71.1              | -  | 659.5    |
| Bi 83   | 1.2                   | ± 0.5               | -  | 208.1    |
| Br 35   | 53.3                  | ± 1.2               | -  | 22045.7  |
| Ca 20   | 79078                 | ± 639               | -  | 120586   |
| Cd 48   | ND <2.8               | ± 2.8               | -  | 0.8      |
| Ce 58   | ND <24.7              | ± 24.7              | -  | 0        |
| Cl 17   | 23246                 | ± 956               | -  | 5142.5   |
| Co 27   | ND <3.9               | ± 3.9               | -  | 0        |
| Cr 24   | 21.3                  | ± 6.7               | -  | 299.3    |
| Cu 29   | 29.8                  | ± 1.6               | -  | 2629.9   |
| Fe 26   | 1320                  | ± 20.9              | -  | 35581.8  |
| Ga 31   | ND <0.6               | ± 0.6               | -  | 0        |
| Ge 32   | ND <0.4               | ± 0.4               | -  | 0        |
| Hf 72   | 36.5                  | ± 3.6               | -  | 1394.3   |
| Hg 80   | ND <0.6               | ± 0.6               | -  | 0        |
| In 49   | ND <2.1               | ± 2.1               | -  | 0        |
| K 19    | 67835                 | ± 735               | -  | 64092.8  |
| La 57   | ND <37.9              | ± 37.9              | -  | 0        |
| Mn 25   | 533                   | ± 16.7              | -  | 9180.8   |
| Mo 42   | 476                   | ± 15.9              | -  | 24       |
| Nd 60   | ND <14.8              | ± 14.8              | -  | 0        |
| Ni 28   | 6.1                   | ± 0.9               | -  | 431.3    |
| P 15    | ND <2211              | ± 2211              | -  | 0        |
| Pb 82   | 2.4                   | ± 0.3               | -  | 591.1    |
| Pd 46   | 3.7                   | ± 2.0               | -  | 0.7      |
| Pr 59   | ND <13.2              | ± 13.2              | -  | 0        |
| Rb 37   | 25.7                  | ± 0.7               | -  | 15077.9  |
| Rh 45   | 5.1                   | ± 2.4               | -  | 0.7      |
| S 16    | 8399                  | ± 986               | -  | 791.6    |
| Sb 51   | ND <3.6               | ± 3.6               | -  | 0        |
| Se 34   | ND <0.3               | ± 0.3               | -  | 0        |
| Si 14   | ND <3398              | ± 3398              | -  | 0        |
| Sn 50   | ND <3.5               | ± 3.5               | -  | 0        |
| Sr 38   | 149                   | ± 1.4               | -  | 100513.8 |
| Ta 73   | ND <2.0               | ± 2.0               | -  | 0        |
| Ti 22   | 338                   | ± 36.4              | -  | 1254.4   |
| Zn 30   | 79.5                  | ± 2.4               | -  | 9787.9   |

## Sample F2

| Element | Concentration<br>/ppm | Uncertainty<br>/ppm | Area<br>Density<br>(ug/cm <sup>2</sup> ) | Counts   |
|---------|-----------------------|---------------------|--|----------|
| Ag 47   | ND <2.3               | ± 2.3               | -  | 0        |
| Al 13   | ND <22369             | ± 22369             | -  | 0        |
| As 33   | ND <0.3               | ± 0.3               | -  | 0        |
| Au 79   | ND <0.8               | ± 0.8               | -  | 0        |
| Ba 56   | 477                   | ± 61.4              | -  | 831.2    |
| Bi 83   | 1                     | ± 0.5               | -  | 178.9    |
| Br 35   | 122                   | ± 1.7               | -  | 52755.7  |
| Ca 20   | 74506                 | ± 626               | -  | 117289.7 |
| Cd 48   | ND <2.8               | ± 2.8               | -  | 0        |
| Ce 58   | ND <24.3              | ± 24.3              | -  | 0        |
| Cl 17   | 19630                 | ± 881               | -  | 4568.2   |
| Co 27   | ND <3.5               | ± 3.5               | -  | 0        |
| Cr 24   | 22.1                  | ± 6.9               | -  | 324.8    |
| Cu 29   | 25                    | ± 1.4               | -  | 2308.1   |
| Fe 26   | 1114                  | ± 18.8              | -  | 31399.8  |
| Ga 31   | ND <0.6               | ± 0.6               | -  | 0        |
| Ge 32   | ND <0.4               | ± 0.4               | -  | 49.5     |
| Hf 72   | 31.5                  | ± 3.3               | -  | 1260.2   |
| Hg 80   | ND <0.4               | ± 0.4               | -  | 0        |
| In 49   | ND <3.4               | ± 3.4               | -  | 0        |
| K 19    | 78408                 | ± 785               | -  | 78543.2  |
| La 57   | ND <37.5              | ± 37.5              | -  | 0        |
| Mn 25   | 324                   | ± 12.9              | -  | 5832.1   |
| Mo 42   | 495                   | ± 16.3              | -  | 26.1     |
| Nd 60   | ND <14.9              | ± 14.9              | -  | 0        |
| Ni 28   | 7.2                   | ± 1.0               | -  | 537.5    |
| P 15    | ND <2143              | ± 2143              | -  | 0        |
| Pb 82   | ND <0.8               | ± 0.8               | -  | 158.7    |
| Pd 46   | ND <2.0               | ± 2.0               | -  | 0        |
| Pr 59   | ND <13.2              | ± 13.2              | -  | 0        |
| Rb 37   | 28.1                  | ± 0.8               | -  | 17240.2  |
| Rh 45   | 4.6                   | ± 2.4               | -  | 0.7      |
| S 16    | 5541                  | ± 856               | -  | 546.3    |
| Sb 51   | ND <3.6               | ± 3.6               | -  | 0        |
| Se 34   | ND <0.3               | ± 0.3               | -  | 0        |
| Si 14   | ND <3248              | ± 3248              | -  | 0        |
| Sn 50   | ND <3.6               | ± 3.6               | -  | 0        |
| Sr 38   | 151                   | ± 1.4               | -  | 106782.6 |
| Ta 73   | ND <1.9               | ± 1.9               | -  | 0        |
| Ti 22   | 155                   | ± 30.4              | -  | 599.5    |
| Zn 30   | 56.8                  | ± 2.0               | -  | 7318.1   |

## Sample G1

| Element | Concentration<br>/ppm | Uncertainty<br>/ppm | Area<br>Density<br>(ug/cm <sup>2</sup> ) | Counts  |
|---------|-----------------------|---------------------|--|---------|
| Ag 47   | ND <2.0               | ± 2.0               | -  | 0       |
| Al 13   | ND <19109             | ± 19109             | -  | 0       |
| As 33   | ND <0.3               | ± 0.3               | -  | 0       |
| Au 79   | ND <0.7               | ± 0.7               | -  | 0       |
| Ba 56   | 346                   | ± 48.2              | -  | 582.2   |
| Bi 83   | ND <0.5               | ± 0.5               | -  | 0       |
| Br 35   | 29.8                  | ± 0.9               | -  | 12730.6 |
| Ca 20   | 53352                 | ± 509               | -  | 77395.7 |
| Cd 48   | ND <2.4               | ± 2.4               | -  | 0       |
| Ce 58   | ND <23.9              | ± 23.9              | -  | 0       |
| Cl 17   | 9067                  | ± 624               | -  | 1736.4  |
| Co 27   | ND <3.5               | ± 3.5               | -  | 0       |
| Cr 24   | 16.2                  | ± 6.2               | -  | 230.3   |
| Cu 29   | 31.2                  | ± 1.6               | -  | 2818.4  |
| Fe 26   | 1092                  | ± 18.8              | -  | 29993.2 |
| Ga 31   | ND <0.6               | ± 0.6               | -  | 0       |
| Ge 32   | ND <0.4               | ± 0.4               | -  | 0       |
| Hf 72   | 41.4                  | ± 3.7               | -  | 1619.9  |
| Hg 80   | ND <0.6               | ± 0.6               | -  | 0       |
| In 49   | ND <1.8               | ± 1.8               | -  | 0       |
| K 19    | 43278                 | ± 587               | -  | 36589.5 |
| La 57   | ND <36.9              | ± 36.9              | -  | 0       |
| Mn 25   | 405                   | ± 14.5              | -  | 7094.4  |
| Mo 42   | 342                   | ± 12.8              | -  | 14.7    |
| Nd 60   | ND <14.4              | ± 14.4              | -  | 0       |
| Ni 28   | 4.8                   | ± 0.8               | -  | 349.6   |
| P 15    | ND <1359              | ± 1359              | -  | 0       |
| Pb 82   | ND <0.8               | ± 0.8               | -  | 137.9   |
| Pd 46   | 3.4                   | ± 1.8               | -  | 0.6     |
| Pr 59   | ND <18.1              | ± 18.1              | -  | 0       |
| Rb 37   | 31.8                  | ± 0.7               | -  | 19281.9 |
| Rh 45   | 4.7                   | ± 2.0               | -  | 0.6     |
| S 16    | ND <631               | ± 631               | -  | 0       |
| Sb 51   | ND <3.0               | ± 3.0               | -  | 0       |
| Se 34   | ND <0.3               | ± 0.3               | -  | 0       |
| Si 14   | ND <2007              | ± 2007              | -  | 0       |
| Sn 50   | ND <3.0               | ± 3.0               | -  | 0       |
| Sr 38   | 135                   | ± 1.3               | -  | 94637.8 |
| Ta 73   | ND <1.9               | ± 1.9               | -  | 0       |
| Ti 22   | 130                   | ± 26.4              | -  | 486.2   |
| Zn 30   | 74.4                  | ± 2.3               | -  | 9414    |

## Sample G2

| Element | Concentration<br>/ppm | Uncertainty<br>/ppm | Area<br>Density<br>(ug/cm <sup>2</sup> ) | Counts  |
|---------|-----------------------|---------------------|--|---------|
| Ag 47   | ND <2.0               | ± 2.0               | -  | 0       |
| Al 13   | ND <20889             | ± 20889             | -  | 0       |
| As 33   | ND <0.2               | ± 0.2               | -  | 0       |
| Au 79   | ND <0.7               | ± 0.7               | -  | 0       |
| Ba 56   | ND <50.7              | ± 50.7              | -  | 0       |
| Bi 83   | ND <0.5               | ± 0.5               | -  | 0       |
| Br 35   | 32                    | ± 0.9               | -  | 14332.9 |
| Ca 20   | 60282                 | ± 546               | -  | 93663   |
| Cd 48   | 2.8                   | ± 2.6               | -  | 0.9     |
| Ce 58   | 56                    | ± 17.5              | -  | 179     |
| Cl 17   | 11287                 | ± 687               | -  | 2379.1  |
| Co 27   | ND <3.2               | ± 3.2               | -  | 0       |
| Cr 24   | 14.6                  | ± 6.0               | -  | 219.5   |
| Cu 29   | 31.5                  | ± 1.6               | -  | 2992.4  |
| Fe 26   | 985                   | ± 17.5              | -  | 28462.4 |
| Ga 31   | ND <0.6               | ± 0.6               | -  | 0       |
| Ge 32   | ND <0.3               | ± 0.3               | -  | 0       |
| Hf 72   | 40.4                  | ± 3.5               | -  | 1661.3  |
| Hg 80   | ND <0.4               | ± 0.4               | -  | 0       |
| In 49   | ND <1.8               | ± 1.8               | -  | 0       |
| K 19    | 51785                 | ± 640               | -  | 47939.4 |
| La 57   | ND <36.0              | ± 36.0              | -  | 0       |
| Mn 25   | 431                   | ± 14.6              | -  | 7953    |
| Mo 42   | 385                   | ± 13.8              | -  | 18.2    |
| Nd 60   | ND <14.3              | ± 14.3              | -  | 0       |
| Ni 28   | 4.6                   | ± 0.8               | -  | 356.1   |
| P 15    | ND <2019              | ± 2019              | -  | 0       |
| Pb 82   | 0.8                   | ± 0.2               | -  | 214.8   |
| Pd 46   | 3.6                   | ± 1.9               | -  | 0.7     |
| Pr 59   | ND <18.1              | ± 18.1              | -  | 0       |
| Rb 37   | 34.2                  | ± 0.7               | -  | 21699.2 |
| Rh 45   | 4.2                   | ± 2.1               | -  | 0.6     |
| S 16    | ND <689               | ± 689               | -  | 0       |
| Sb 51   | ND <3.2               | ± 3.2               | -  | 0       |
| Se 34   | 0.5                   | ± 0.3               | -  | 173.5   |
| Si 14   | ND <2231              | ± 2231              | -  | 0       |
| Sn 50   | ND <3.2               | ± 3.2               | -  | 0       |
| Sr 38   | 136                   | ± 1.3               | -  | 99591.1 |
| Ta 73   | ND <1.9               | ± 1.9               | -  | 0       |
| Ti 22   | 177                   | ± 24.5              | -  | 695     |
| Zn 30   | 72.7                  | ± 2.2               | -  | 9652.1  |

# Sample H1

| Element | Concentration<br>/ppm | Uncertainty<br>/ppm | Area<br>Density<br>(ug/cm <sup>2</sup> ) | Counts   |
|---------|-----------------------|---------------------|--|----------|
| Ag 47   | ND <2.2               | ± 2.2               | -  | 0        |
| Al 13   | ND <22130             | ± 22130             | -  | 0        |
| As 33   | ND <0.3               | ± 0.3               | -  | 0        |
| Au 79   | ND <0.8               | ± 0.8               | -  | 0        |
| Ba 56   | 616                   | ± 75.7              | -  | 1015     |
| Bi 83   | 1.3                   | ± 0.5               | -  | 225.1    |
| Br 35   | 143                   | ± 1.9               | -  | 58165.6  |
| Ca 20   | 75706                 | ± 640               | -  | 112812.8 |
| Cd 48   | 4.1                   | ± 2.8               | -  | 1.4      |
| Ce 58   | ND <25.4              | ± 25.4              | -  | 0        |
| Cl 17   | 16352                 | ± 818               | -  | 3624.7   |
| Co 27   | ND <3.7               | ± 3.7               | -  | 0        |
| Cr 24   | 16.8                  | ± 6.7               | -  | 232.1    |
| Cu 29   | 24.5                  | ± 1.4               | -  | 2124.8   |
| Fe 26   | 1264                  | ± 20.6              | -  | 33575.6  |
| Ga 31   | ND <0.6               | ± 0.6               | -  | 0        |
| Ge 32   | ND <0.4               | ± 0.4               | -  | 0        |
| Hf 72   | 37                    | ± 3.6               | -  | 1391.4   |
| Hg 80   | ND <0.6               | ± 0.6               | -  | 0        |
| In 49   | ND <2.0               | ± 2.0               | -  | 0        |
| K 19    | 83430                 | ± 816               | -  | 80172.4  |
| La 57   | ND <41.8              | ± 41.8              | -  | 0        |
| Mn 25   | 425                   | ± 15.1              | -  | 7219.6   |
| Mo 42   | 460                   | ± 15.7              | -  | 23.1     |
| Nd 60   | ND <15.8              | ± 15.8              | -  | 0        |
| Ni 28   | 3.8                   | ± 0.7               | -  | 268.1    |
| P 15    | ND <2189              | ± 2189              | -  | 0        |
| Pb 82   | 1.2                   | ± 0.3               | -  | 290.5    |
| Pd 46   | 3.7                   | ± 2.0               | -  | 0.7      |
| Pr 59   | ND <19.5              | ± 19.5              | -  | 0        |
| Rb 37   | 34.8                  | ± 0.9               | -  | 20100.9  |
| Rh 45   | 4.2                   | ± 2.3               | -  | 0.6      |
| S 16    | 4847                  | ± 830               | -  | 454.5    |
| Sb 51   | ND <3.4               | ± 3.4               | -  | 0        |
| Se 34   | ND <0.3               | ± 0.3               | -  | 0        |
| Si 14   | ND <3675              | ± 3675              | -  | 0        |
| Sn 50   | ND <3.4               | ± 3.4               | -  | 0        |
| Sr 38   | 166                   | ± 1.5               | -  | 110449.7 |
| Ta 73   | ND <2.1               | ± 2.1               | -  | 0        |
| Ti 22   | 296                   | ± 37.8              | -  | 1081.4   |
| Zn 30   | 64.6                  | ± 2.2               | -  | 7836.5   |

## Sample H2

| Element | Concentration<br>/ppm | Uncertainty<br>/ppm | Area<br>Density<br>(ug/cm <sup>2</sup> ) | Counts  |
|---------|-----------------------|---------------------|--|---------|
| Ag 47   | ND <2.0               | ± 2.0               | -  | 0       |
| Al 13   | ND <19291             | ± 19291             | -  | 0       |
| As 33   | 0.2                   | ± 0.1               | -  | 45.6    |
| Au 79   | ND <0.7               | ± 0.7               | -  | 0       |
| Ba 56   | 276                   | ± 53.8              | -  | 448.8   |
| Bi 83   | ND <0.5               | ± 0.5               | -  | 0       |
| Br 35   | 37.9                  | ± 1.0               | -  | 15578.4 |
| Ca 20   | 54492                 | ± 522               | -  | 76637   |
| Cd 48   | ND <2.5               | ± 2.5               | -  | 0.7     |
| Ce 58   | ND <24.6              | ± 24.6              | -  | 0       |
| Cl 17   | 12172                 | ± 710               | -  | 2350.3  |
| Co 27   | ND <3.5               | ± 3.5               | -  | 0       |
| Cr 24   | 22.5                  | ± 6.6               | -  | 309.4   |
| Cu 29   | 25.8                  | ± 1.5               | -  | 2251.7  |
| Fe 26   | 1131                  | ± 19.5              | -  | 30025.1 |
| Ga 31   | ND <0.6               | ± 0.6               | -  | 0       |
| Ge 32   | ND <0.3               | ± 0.3               | -  | 0       |
| Hf 72   | 42.1                  | ± 3.7               | -  | 1591.5  |
| Hg 80   | ND <0.6               | ± 0.6               | -  | 0       |
| In 49   | ND <2.9               | ± 2.9               | -  | 0       |
| K 19    | 55997                 | ± 665               | -  | 47397.7 |
| La 57   | ND <39.1              | ± 39.1              | -  | 0       |
| Mn 25   | 475                   | ± 15.9              | -  | 8045.6  |
| Mo 42   | 346                   | ± 13.0              | -  | 15      |
| Nd 60   | ND <15.2              | ± 15.2              | -  | 0       |
| Ni 28   | 5.4                   | ± 0.8               | -  | 382.6   |
| P 15    | ND <1344              | ± 1344              | -  | 0       |
| Pb 82   | 1.7                   | ± 0.2               | -  | 416.6   |
| Pd 46   | ND <1.7               | ± 1.7               | -  | 0       |
| Pr 59   | ND <18.8              | ± 18.8              | -  | 0       |
| Rb 37   | 22.3                  | ± 0.6               | -  | 13020.5 |
| Rh 45   | 3.9                   | ± 2.0               | -  | 0.5     |
| S 16    | ND <719               | ± 719               | -  | 0       |
| Sb 51   | ND <3.1               | ± 3.1               | -  | 0       |
| Se 34   | ND <0.3               | ± 0.3               | -  | 0       |
| Si 14   | ND <2193              | ± 2193              | -  | 0       |
| Sn 50   | ND <3.1               | ± 3.1               | -  | 0       |
| Sr 38   | 106                   | ± 1.2               | -  | 71313.2 |
| Ta 73   | ND <2.0               | ± 2.0               | -  | 0       |
| Ti 22   | 167                   | ± 27.5              | -  | 605.3   |
| Zn 30   | 71.7                  | ± 2.3               | -  | 8746.8  |

# Sample I

| Element | Concentration<br>/ppm | Uncertainty<br>/ppm | Area<br>Density<br>(ug/cm <sup>2</sup> ) | Counts  |
|---------|-----------------------|---------------------|--|---------|
| Ag 47   | ND <2.0               | ± 2.0               | -  | 0       |
| Al 13   | ND <20255             | ± 20255             | -  | 0       |
| As 33   | ND <0.2               | ± 0.2               | -  | 0       |
| Au 79   | ND <0.8               | ± 0.8               | -  | 0       |
| Ba 56   | 522                   | ± 58.2              | -  | 916.9   |
| Bi 83   | 0.9                   | ± 0.5               | -  | 167.8   |
| Br 35   | 118                   | ± 1.6               | -  | 52368.9 |
| Ca 20   | 45415                 | ± 474               | -  | 67289.8 |
| Cd 48   | ND <2.3               | ± 2.3               | -  | 0       |
| Ce 58   | 120                   | ± 21.4              | -  | 379.6   |
| Cl 17   | 5536                  | ± 503               | -  | 1091.4  |
| Co 27   | ND <3.6               | ± 3.6               | -  | 0       |
| Cr 24   | 34.1                  | ± 7.5               | -  | 507.2   |
| Cu 29   | 24.3                  | ± 1.4               | -  | 2288.8  |
| Fe 26   | 1269                  | ± 19.8              | -  | 36374.4 |
| Ga 31   | ND <0.6               | ± 0.6               | -  | 0       |
| Ge 32   | 1.1                   | ± 0.4               | -  | 244.7   |
| Hf 72   | 42.6                  | ± 3.5               | -  | 1738.2  |
| Hg 80   | ND <0.6               | ± 0.6               | -  | 0       |
| In 49   | ND <1.7               | ± 1.7               | -  | 0       |
| K 19    | 49414                 | ± 625               | -  | 43337.2 |
| La 57   | ND <35.8              | ± 35.8              | -  | 0       |
| Mn 25   | 333                   | ± 13.1              | -  | 6080.2  |
| Mo 42   | 334                   | ± 12.6              | -  | 14.8    |
| Nd 60   | ND <14.8              | ± 14.8              | -  | 0       |
| Ni 28   | 9.6                   | ± 1.1               | -  | 731.6   |
| P 15    | ND <1279              | ± 1279              | -  | 0       |
| Pb 82   | ND <0.7               | ± 0.7               | -  | 0       |
| Pd 46   | ND <1.7               | ± 1.7               | -  | 0       |
| Pr 59   | ND <12.7              | ± 12.7              | -  | 0       |
| Rb 37   | 17                    | ± 0.6               | -  | 10765.9 |
| Rh 45   | 3.1                   | ± 1.9               | -  | 0.4     |
| S 16    | ND <615               | ± 615               | -  | 0       |
| Sb 51   | ND <2.9               | ± 2.9               | -  | 0       |
| Se 34   | ND <0.3               | ± 0.3               | -  | 0       |
| Si 14   | ND <2121              | ± 2121              | -  | 0       |
| Sn 50   | ND <2.9               | ± 2.9               | -  | 0       |
| Sr 38   | 93.4                  | ± 1.1               | -  | 68061.7 |
| Ta 73   | ND <1.9               | ± 1.9               | -  | 0       |
| Ti 22   | 293                   | ± 29.3              | -  | 1144.1  |
| Zn 30   | 57.1                  | ± 2.0               | -  | 7530.8  |

## Sample J

| Element | Concentration<br>/ppm | Uncertainty<br>/ppm | Area<br>Density<br>(ug/cm <sup>2</sup> ) | Counts   |
|---------|-----------------------|---------------------|--|----------|
| Ag 47   | ND <2.2               | ± 2.2               | -  | 0        |
| Al 13   | ND <21078             | ± 21078             | -  | 0        |
| As 33   | ND <0.2               | ± 0.2               | -  | 0        |
| Au 79   | ND <0.7               | ± 0.7               | -  | 0        |
| Ba 56   | 518                   | ± 72.6              | -  | 934.2    |
| Bi 83   | 1                     | ± 0.5               | -  | 187.6    |
| Br 35   | 73.2                  | ± 1.3               | -  | 33240.9  |
| Ca 20   | 54565                 | ± 524               | -  | 84990    |
| Cd 48   | ND <2.6               | ± 2.6               | -  | 0        |
| Ce 58   | ND <24.6              | ± 24.6              | -  | 0        |
| Cl 17   | 9783                  | ± 644               | -  | 2098.1   |
| Co 27   | ND <3.5               | ± 3.5               | -  | 0        |
| Cr 24   | 60.1                  | ± 9.0               | -  | 915.8    |
| Cu 29   | 27.4                  | ± 1.5               | -  | 2642.7   |
| Fe 26   | 1273                  | ± 19.6              | -  | 37337.9  |
| Ga 31   | ND <0.6               | ± 0.6               | -  | 0        |
| Ge 32   | ND <0.4               | ± 0.4               | -  | 0        |
| Hf 72   | 37.7                  | ± 3.4               | -  | 1574.1   |
| Hg 80   | ND <0.6               | ± 0.6               | -  | 0        |
| In 49   | ND <1.9               | ± 1.9               | -  | 0        |
| K 19    | 59013                 | ± 682               | -  | 55763.2  |
| La 57   | ND <38.6              | ± 38.6              | -  | 0        |
| Mn 25   | 255                   | ± 11.4              | -  | 4770.4   |
| Mo 42   | 393                   | ± 13.9              | -  | 18.9     |
| Nd 60   | ND <14.5              | ± 14.5              | -  | 0        |
| Ni 28   | 7.8                   | ± 1.0               | -  | 609.1    |
| P 15    | ND <1348              | ± 1348              | -  | 0        |
| Pb 82   | ND <0.7               | ± 0.7               | -  | 0        |
| Pd 46   | 5.6                   | ± 2.1               | -  | 1.1      |
| Pr 59   | ND <19.7              | ± 19.7              | -  | 0        |
| Rb 37   | 27.9                  | ± 0.7               | -  | 17975.7  |
| S 16    | ND <612               | ± 612               | -  | 0        |
| Sb 51   | ND <3.3               | ± 3.3               | -  | 0        |
| Se 34   | 0.5                   | ± 0.3               | -  | 190.8    |
| Si 14   | ND <2220              | ± 2220              | -  | 0        |
| Sn 50   | ND <3.2               | ± 3.2               | -  | 0        |
| Sr 38   | 153                   | ± 1.4               | -  | 113536.5 |
| Ta 73   | ND <1.9               | ± 1.9               | -  | 0        |
| Ti 22   | 350                   | ± 36.9              | -  | 1402.4   |
| Zn 30   | 62.5                  | ± 2.0               | -  | 8425.4   |

## Sample K

| Element | Concentration<br>/ppm | Uncertainty<br>/ppm | Area<br>Density<br>(ug/cm <sup>2</sup> ) | Counts   |
|---------|-----------------------|---------------------|--|----------|
| Ag 47   | ND <2.3               | ± 2.3               | -  | 0        |
| Al 13   | ND <19803             | ± 19803             | -  | 0        |
| As 33   | ND <0.2               | ± 0.2               | -  | 0        |
| Au 79   | ND <0.7               | ± 0.7               | -  | 0        |
| Ba 56   | ND <168               | ± 168               | -  | 0        |
| Bi 83   | 0.9                   | ± 0.5               | -  | 178.7    |
| Br 35   | 132                   | ± 1.7               | -  | 63501.7  |
| Ca 20   | 63533                 | ± 559               | -  | 107694.3 |
| Cd 48   | ND <2.6               | ± 2.6               | -  | 0        |
| Ce 58   | 133                   | ± 22.7              | -  | 459.1    |
| Cl 17   | 7742                  | ± 583               | -  | 1765.3   |
| Co 27   | ND <3.5               | ± 3.5               | -  | 0        |
| Cr 24   | 63.3                  | ± 9.3               | -  | 1025.7   |
| Cu 29   | 31.1                  | ± 1.5               | -  | 3183.4   |
| Fe 26   | 1427                  | ± 20.1              | -  | 44519.9  |
| Ga 31   | ND <0.5               | ± 0.5               | -  | 0        |
| Ge 32   | ND <0.4               | ± 0.4               | -  | 0        |
| Hf 72   | 32.3                  | ± 3.2               | -  | 1431.8   |
| Hg 80   | ND <0.4               | ± 0.4               | -  | 0        |
| In 49   | ND <2.0               | ± 2.0               | -  | 0        |
| K 19    | 51154                 | ± 635               | -  | 51618.8  |
| La 57   | ND <35.3              | ± 35.3              | -  | 0        |
| Mn 25   | 311                   | ± 12.1              | -  | 6184.2   |
| Mo 42   | 398                   | ± 14.0              | -  | 20.3     |
| Nd 60   | ND <14.0              | ± 14.0              | -  | 0        |
| Ni 28   | 10.6                  | ± 1.1               | -  | 877.3    |
| P 15    | ND <1428              | ± 1428              | -  | 0        |
| Pb 82   | ND <0.7               | ± 0.7               | -  | 0        |
| Pd 46   | ND <1.8               | ± 1.8               | -  | 0        |
| Pr 59   | ND <12.4              | ± 12.4              | -  | 0        |
| Rb 37   | 23.3                  | ± 0.7               | -  | 15910.7  |
| S 16    | ND <692               | ± 692               | -  | 0        |
| Sb 51   | ND <3.4               | ± 3.4               | -  | 0        |
| Se 34   | ND <0.3               | ± 0.3               | -  | 0        |
| Si 14   | ND <2306              | ± 2306              | -  | 0        |
| Sn 50   | ND <3.5               | ± 3.5               | -  | 0        |
| Sr 38   | 117                   | ± 1.2               | -  | 91945.7  |
| Ta 73   | ND <1.8               | ± 1.8               | -  | 0        |
| Ti 22   | 346                   | ± 32.0              | -  | 1472.2   |
| Zn 30   | 54.2                  | ± 1.8               | -  | 7753.4   |

## Sample L

| Element | Concentration<br>/ppm | Uncertainty<br>/ppm | Area<br>Density<br>(ug/cm <sup>2</sup> ) | Counts   |
|---------|-----------------------|---------------------|--|----------|
| Ag 47   | ND <2.4               | ± 2.4               | -  | 0        |
| Al 13   | ND <18885             | ± 18885             | -  | 0        |
| As 33   | ND <0.2               | ± 0.2               | -  | 0        |
| Au 79   | ND <0.7               | ± 0.7               | -  | 0        |
| Ba 56   | 131                   | ± 50.3              | -  | 261      |
| Bi 83   | ND <0.4               | ± 0.4               | -  | 0        |
| Br 35   | 62.8                  | ± 1.1               | -  | 31996    |
| Ca 20   | 52964                 | ± 504               | -  | 91288.8  |
| Cd 48   | 3.4                   | ± 2.9               | -  | 1.2      |
| Ce 58   | 92.9                  | ± 19.5              | -  | 335.6    |
| Cl 17   | 9723                  | ± 644               | -  | 2179.8   |
| Co 27   | ND <3.2               | ± 3.2               | -  | 0        |
| Cr 24   | 24.2                  | ± 6.6               | -  | 410.4    |
| Cu 29   | 25                    | ± 1.3               | -  | 2698.9   |
| Fe 26   | 1064                  | ± 17.0              | -  | 34786.7  |
| Ga 31   | ND <0.5               | ± 0.5               | -  | 0        |
| Ge 32   | ND <0.4               | ± 0.4               | -  | 70.6     |
| Hf 72   | 32.6                  | ± 3.1               | -  | 1522.2   |
| Hg 80   | ND <0.3               | ± 0.3               | -  | 0        |
| In 49   | ND <3.3               | ± 3.3               | -  | 0        |
| K 19    | 37050                 | ± 545               | -  | 36619.1  |
| La 57   | ND <34.5              | ± 34.5              | -  | 0        |
| Mn 25   | 239                   | ± 10.5              | -  | 4989.6   |
| Mo 42   | 447                   | ± 14.6              | -  | 22.5     |
| Nd 60   | ND <13.2              | ± 13.2              | -  | 0        |
| Ni 28   | 7                     | ± 0.9               | -  | 609.6    |
| P 15    | ND <1936              | ± 1936              | -  | 0        |
| Pb 82   | 1.1                   | ± 0.3               | -  | 337.1    |
| Pd 46   | 4.4                   | ± 2.1               | -  | 0.9      |
| Pr 59   | ND <12.0              | ± 12.0              | -  | 0        |
| Rb 37   | 28.4                  | ± 0.7               | -  | 20545.8  |
| Rh 45   | 3.7                   | ± 2.2               | -  | 0.5      |
| S 16    | ND <596               | ± 596               | -  | 0        |
| Sb 51   | ND <3.6               | ± 3.6               | -  | 0        |
| Se 34   | ND <0.3               | ± 0.3               | -  | 0        |
| Si 14   | ND <2174              | ± 2174              | -  | 0        |
| Sn 50   | ND <3.6               | ± 3.6               | -  | 0        |
| Sr 38   | 129                   | ± 1.2               | -  | 107970.4 |
| Ta 73   | ND <1.7               | ± 1.7               | -  | 0        |
| Ti 22   | 278                   | ± 28.3              | -  | 1234.5   |
| Zn 30   | 49.2                  | ± 1.7               | -  | 7410.3   |

## Sample M

| Element | Concentration<br>/ppm | Uncertainty<br>/ppm | Area<br>Density<br>(ug/cm <sup>2</sup> ) | Counts   |
|---------|-----------------------|---------------------|--|----------|
| Ag 47   | ND <2.3               | ± 2.3               | -  | 0        |
| Al 13   | ND <19643             | ± 19643             | -  | 0        |
| As 33   | ND <0.2               | ± 0.2               | -  | 0        |
| Au 79   | ND <0.6               | ± 0.6               | -  | 0        |
| Ba 56   | 600                   | ± 62.4              | -  | 1179.4   |
| Bi 83   | ND <0.5               | ± 0.5               | -  | 0        |
| Br 35   | 59.3                  | ± 1.1               | -  | 29446.4  |
| Ca 20   | 68495                 | ± 576               | -  | 120863.3 |
| Cd 48   | ND <2.8               | ± 2.8               | -  | 0        |
| Ce 58   | ND <26.6              | ± 26.6              | -  | 0        |
| Cl 17   | 4895                  | ± 481               | -  | 1144.4   |
| Co 27   | ND <2.4               | ± 2.4               | -  | 0        |
| Cr 24   | 25.1                  | ± 7.0               | -  | 417.7    |
| Cu 29   | 23.4                  | ± 1.3               | -  | 2469.1   |
| Fe 26   | 434                   | ± 11.2              | -  | 13866.3  |
| Ga 31   | ND <0.5               | ± 0.5               | -  | 0        |
| Ge 32   | ND <0.3               | ± 0.3               | -  | 0        |
| Hf 72   | 32.1                  | ± 3.1               | -  | 1466.4   |
| Hg 80   | ND <0.3               | ± 0.3               | -  | 0        |
| In 49   | ND <2.1               | ± 2.1               | -  | 0        |
| K 19    | 47397                 | ± 611               | -  | 49342.2  |
| La 57   | ND <35.3              | ± 35.3              | -  | 0        |
| Mn 25   | 263                   | ± 11.1              | -  | 5374.1   |
| Mo 42   | 449                   | ± 14.9              | -  | 23.5     |
| Nd 60   | ND <14.2              | ± 14.2              | -  | 0        |
| Ni 28   | 6.4                   | ± 0.9               | -  | 546.4    |
| P 15    | ND <2112              | ± 2112              | -  | 0        |
| Pb 82   | ND <0.7               | ± 0.7               | -  | 0        |
| Pd 46   | 5.6                   | ± 2.2               | -  | 1.1      |
| Pr 59   | ND <17.7              | ± 17.7              | -  | 0        |
| Rb 37   | 4.9                   | ± 0.4               | -  | 3426.9   |
| Rh 45   | 5.5                   | ± 2.3               | -  | 0.8      |
| S 16    | ND <643               | ± 643               | -  | 0        |
| Sb 51   | ND <3.6               | ± 3.6               | -  | 0        |
| Se 34   | ND <0.3               | ± 0.3               | -  | 0        |
| Si 14   | ND <2261              | ± 2261              | -  | 0        |
| Sn 50   | ND <3.5               | ± 3.5               | -  | 0        |
| Sr 38   | 168                   | ± 1.4               | -  | 136411.3 |
| Ta 73   | ND <1.8               | ± 1.8               | -  | 0        |
| Ti 22   | 140                   | ± 29.8              | -  | 610.6    |
| Zn 30   | 105                   | ± 2.5               | -  | 15529.2  |

Sample N

| Element | Concentration /ppm | Uncertainty /ppm | Area Density (ug/cm <sup>2</sup> ) | Counts   |
|---------|--------------------|------------------|------------------------------------|----------|
| Ag 47   | ND <2.3            | ± 2.3            | -                                  | 0        |
| Al 13   | ND <21829          | ± 21829          | -                                  | 0        |
| As 33   | ND <0.2            | ± 0.2            | -                                  | 0        |
| Au 79   | ND <0.7            | ± 0.7            | -                                  | 0        |
| Ba 56   | 620                | ± 52.6           | -                                  | 1124.3   |
| Bi 83   | ND <0.5            | ± 0.5            | -                                  | 0        |
| Br 35   | 62.1               | ± 1.2            | -                                  | 28355.3  |
| Ca 20   | 36424              | ± 447            | -                                  | 54255.7  |
| Cd 48   | 3.1                | ± 2.8            | -                                  | 1        |
| Ce 58   | ND <24.3           | ± 24.3           | -                                  | 0        |
| Cl 17   | 16724              | ± 818            | -                                  | 3689.6   |
| Co 27   | ND <2.4            | ± 2.4            | -                                  | 0        |
| Cr 24   | 37.4               | ± 7.7            | -                                  | 572.4    |
| Cu 29   | 25.4               | ± 1.4            | -                                  | 2465.1   |
| Fe 26   | 382                | ± 11.4           | -                                  | 11260.1  |
| Ga 31   | ND <0.5            | ± 0.5            | -                                  | 0        |
| Ge 32   | ND <0.4            | ± 0.4            | -                                  | 0        |
| Hf 72   | 36.4               | ± 3.4            | -                                  | 1527.8   |
| Hg 80   | ND <0.4            | ± 0.4            | -                                  | 0        |
| In 49   | ND <2.0            | ± 2.0            | -                                  | 0        |
| K 19    | 83656              | ± 810            | -                                  | 80070.3  |
| La 57   | ND <23.6           | ± 23.6           | -                                  | 0        |
| Mn 25   | 1008               | ± 21.7           | -                                  | 18981.6  |
| Mo 42   | 420                | ± 14.4           | -                                  | 20.8     |
| Nd 60   | ND <14.5           | ± 14.5           | -                                  | 0        |
| Ni 28   | 7.8                | ± 1.0            | -                                  | 606.6    |
| P 15    | ND <1605           | ± 1605           | -                                  | 0        |
| Pb 82   | ND <0.7            | ± 0.7            | -                                  | 0        |
| Pd 46   | 3.9                | ± 2.0            | -                                  | 0.7      |
| Pr 59   | ND <18.5           | ± 18.5           | -                                  | 0        |
| Rb 37   | 22.1               | ± 0.6            | -                                  | 14357.4  |
| Rh 45   | 3.9                | ± 2.2            | -                                  | 0.6      |
| S 16    | ND <571            | ± 571            | -                                  | 0        |
| Sb 51   | ND <3.4            | ± 3.4            | -                                  | 0        |
| Se 34   | ND <0.3            | ± 0.3            | -                                  | 0        |
| Si 14   | ND <3117           | ± 3117           | -                                  | 0        |
| Sn 50   | ND <3.3            | ± 3.3            | -                                  | 0        |
| Sr 38   | 181                | ± 1.5            | -                                  | 135080.5 |
| Ta 73   | ND <1.8            | ± 1.8            | -                                  | 0        |
| Ti 22   | ND <16.0           | ± 16.0           | -                                  | 0        |
| Zn 30   | 81.1               | ± 2.3            | -                                  | 10990.8  |

## Sample O

| Element | Concentration<br>/ppm | Uncertainty<br>/ppm | Area<br>Density<br>(ug/cm <sup>2</sup> ) | Counts  |
|---------|-----------------------|---------------------|--|---------|
| Ag 47   | ND <1.9               | ± 1.9               | -  | 0       |
| Al 13   | ND <18618             | ± 18618             | -  | 0       |
| As 33   | ND <0.2               | ± 0.2               | -  | 0       |
| Au 79   | ND <0.7               | ± 0.7               | -  | 0       |
| Ba 56   | 399                   | ± 51.9              | -  | 703     |
| Bi 83   | ND <0.5               | ± 0.5               | -  | 0       |
| Br 35   | 55.1                  | ± 1.1               | -  | 24768.6 |
| Ca 20   | 56005                 | ± 516               | -  | 85879.7 |
| Cd 48   | ND <2.4               | ± 2.4               | -  | 0       |
| Ce 58   | ND <23.6              | ± 23.6              | -  | 0       |
| Cl 17   | 12462                 | ± 722               | -  | 2472.8  |
| Co 27   | ND <3.1               | ± 3.1               | -  | 0       |
| Cr 24   | 47.2                  | ± 8.1               | -  | 705.1   |
| Cu 29   | 30.1                  | ± 1.6               | -  | 2864.7  |
| Fe 26   | 815                   | ± 16.0              | -  | 23496.3 |
| Ga 31   | ND <0.5               | ± 0.5               | -  | 0       |
| Ge 32   | 0.8                   | ± 0.4               | -  | 168.2   |
| Hf 72   | 40.4                  | ± 3.5               | -  | 1665.2  |
| Hg 80   | 1                     | ± 0.5               | -  | 168     |
| In 49   | ND <1.8               | ± 1.8               | -  | 0       |
| K 19    | 32861                 | ± 515               | -  | 28582.2 |
| La 57   | ND <36.5              | ± 36.5              | -  | 0       |
| Mn 25   | 376                   | ± 13.8              | -  | 6915.7  |
| Mo 42   | 352                   | ± 12.9              | -  | 15.7    |
| Nd 60   | ND <10.0              | ± 10.0              | -  | 0       |
| Ni 28   | 56.9                  | ± 2.5               | -  | 4354.5  |
| P 15    | ND <1971              | ± 1971              | -  | 0       |
| Pb 82   | ND <0.7               | ± 0.7               | -  | 0       |
| Pd 46   | 3.7                   | ± 1.8               | -  | 0.6     |
| Pr 59   | ND <18.3              | ± 18.3              | -  | 0       |
| Rb 37   | 5.1                   | ± 0.4               | -  | 3273.8  |
| Rh 45   | 4.2                   | ± 2.0               | -  | 0.6     |
| S 16    | ND <711               | ± 711               | -  | 0       |
| Sb 51   | ND <3.1               | ± 3.1               | -  | 0       |
| Se 34   | 1.1                   | ± 0.3               | -  | 386.1   |
| Si 14   | ND <2198              | ± 2198              | -  | 0       |
| Sn 50   | ND <3.0               | ± 3.0               | -  | 0       |
| Sr 38   | 74                    | ± 1.0               | -  | 54438.7 |
| Ta 73   | ND <1.9               | ± 1.9               | -  | 0       |
| Ti 22   | 95.6                  | ± 25.7              | -  | 374.6   |
| Zn 30   | 61.8                  | ± 2.0               | -  | 8219.2  |

## Sample P

| Element | Concentration<br>/ppm | Uncertainty<br>/ppm | Area<br>Density<br>(ug/cm <sup>2</sup> ) | Counts   |
|---------|-----------------------|---------------------|--|----------|
| Ag 47   | ND <1.8               | ± 1.8               | -  | 0        |
| Al 13   | ND <20591             | ± 20591             | -  | 0        |
| As 33   | ND <0.3               | ± 0.3               | -  | 0        |
| Au 79   | ND <0.8               | ± 0.8               | -  | 0        |
| Ba 56   | 684                   | ± 56.8              | -  | 930.5    |
| Bi 83   | ND <0.6               | ± 0.6               | -  | 0        |
| Br 35   | 81.3                  | ± 5.1               | -  | 27583.2  |
| Ca 20   | 83442                 | ± 641               | -  | 105493.9 |
| Cd 48   | ND <2.1               | ± 2.1               | -  | 0        |
| Ce 58   | ND <28.9              | ± 28.9              | -  | 0        |
| Cl 17   | 4653                  | ± 473               | -  | 804.8    |
| Co 27   | ND <3.1               | ± 3.1               | -  | 0        |
| Cr 24   | 36.3                  | ± 8.0               | -  | 415.7    |
| Cu 29   | 50.8                  | ± 2.3               | -  | 3674.2   |
| Fe 26   | 469                   | ± 14.0              | -  | 10323.2  |
| Ga 31   | ND <0.7               | ± 0.7               | -  | 0        |
| Ge 32   | ND <0.5               | ± 0.5               | -  | 0        |
| Hf 72   | 51.2                  | ± 4.6               | -  | 1603.3   |
| Hg 80   | ND <0.4               | ± 0.4               | -  | 0        |
| In 49   | ND <2.5               | ± 2.5               | -  | 0        |
| K 19    | 59349                 | ± 678               | -  | 45723    |
| La 57   | ND <39.8              | ± 39.8              | -  | 0        |
| Mn 25   | 278                   | ± 13.7              | -  | 3904.2   |
| Mo 42   | 301                   | ± 12.5              | -  | 11.7     |
| Nd 60   | ND <17.7              | ± 17.7              | -  | 0        |
| Ni 28   | 8.9                   | ± 1.2               | -  | 521.9    |
| P 15    | ND <1565              | ± 1565              | -  | 0        |
| Pb 82   | ND <0.9               | ± 0.9               | -  | 0        |
| Pd 46   | ND <1.5               | ± 1.5               | -  | 0        |
| Pr 59   | ND <22.6              | ± 22.6              | -  | 0        |
| Rb 37   | 5                     | ± 0.5               | -  | 2385.7   |
| Rh 45   | 3.6                   | ± 1.9               | -  | 0.4      |
| S 16    | ND <658               | ± 658               | -  | 0        |
| Sb 51   | ND <2.7               | ± 2.7               | -  | 0        |
| Se 34   | ND <0.3               | ± 0.3               | -  | 0        |
| Si 14   | ND <2324              | ± 2324              | -  | 0        |
| Sn 50   | ND <2.6               | ± 2.6               | -  | 0        |
| Sr 38   | 185                   | ± 1.7               | -  | 102968.7 |
| Ta 73   | ND <2.4               | ± 2.4               | -  | 0        |
| Ti 22   | 70.7                  | ± 30.5              | -  | 213.7    |
| Zn 30   | 166                   | ± 3.7               | -  | 16741.9  |