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Environmental Analysis of Toxic Metals Produced by Cigarette Smoking

Senior Honors Thesis

Spring 2010

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Abstract:

Trace metal elements introduced into our environment from anthropogenic sources can become toxic at high levels contributing to a host of human and animal health problems. The purpose of this work is to initially characterize toxic metals present in cigarette tobacco and ash using Electrothermal Atomic Absorption Spectroscopy (ETAAS). The broader impact of this study is to assess the environmental effects of cigarette smoking around designated smoking areas on the Longwood University campus. Smokers may not be informed about the potential harm to the environment from “ashing” directly on the ground. If the toxic metals present in cigarette ash are not completely volatilized during smoking, they could accumulate over time in the soil adjacent to campus-designated smoking areas. The area surrounding the smoking facilities could, therefore, serve as a starting point for the introduction of toxic metals into the food chain, ground water, or nearby storm water system.

Introduction:

Environmental contamination of soil and water has become an increasing concern in industrialized countries. Metal elements, introduced into our environment from anthropogenic sources, are essential nutrients at trace levels. However, at high levels they become toxic and can contribute to a host of human and animal health problems. If the heavy metals found in cigarettes (tobacco and paper) are not completely volatilized and inhaled during the smoking process, they could accumulate over time in the soil, serving as a starting point for the introduction of toxic metals into the food chain (both aquatic and terrestrial), ground water, or nearby storm water system.

On June 1, 2007, Longwood University implemented a new smoking policy in which individuals are required to smoke in designated outdoor smoking locations on campus. Figure 1 shows the locations of the 14 designated smoking locations in and around the campus. According to Policy #5234 – Campus Non-Smoking Policy, the purpose of creating designated smoking areas on campus is “to promote healthy lifestyles as well as to protect students, faculty, and staff from secondhand smoke, while addressing the growing litter problem on campus that is directly related to smoking [2].” However, due to the potential high volume of smoking and cigarette ash accumulated in these particular locations, the 14 campus smoking sites could serve as the starting point for heavy metal pollution, which can in turn create adverse environmental issues and human and animal health problems.

Environmental Problems Associated with Heavy Metal Contamination:

For many decades, heavy metals in air, soil, and water have been a growing problem plaguing many of the world’s most industrialized countries. Heavy metals, defined as any metallic element with a high density, are extremely harmful to the environment due to the fact

Figure 1. Smoking Locations on the Longwood University Campus [1]



that these metals bioaccumulate [3]. In other words, the concentration of heavy metals can increase at a rate much greater than the rate in which they degrade in the environment.

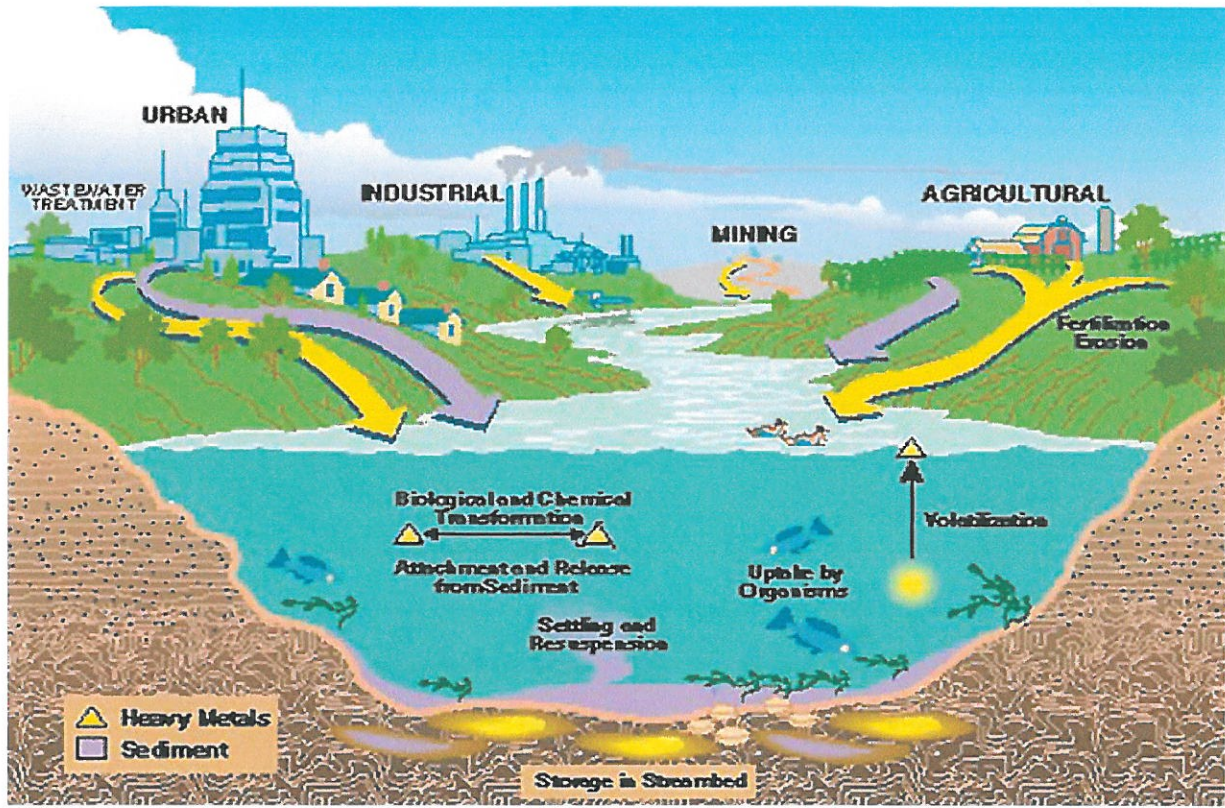
Unfortunately, these toxic metals do not decay, unlike some pollutants [3]. Due to this growing problem, state and federal governments passed laws and regulations in order to protect the surface and ground water from many toxic heavy metals, such as cadmium, zinc, copper, lead, and nickel [4].

Heavy metals can be introduced into the environment through a variety of ways, such as industry, mining, agriculture, and automobiles and roadways. Currently, automobiles and roadways are considered to be the largest source of heavy metal contamination in the environment [5]. Figure 2 depicts the heavy metal pollution cycle and shows these various starting points for the introduction of heavy metals into the environment. As seen in the figure, heavy metals often localize in the bottom of rivers and watersheds, and some metals can volatilize into the atmosphere. As heavy metal concentrations increase in the environment, these metals become increasingly toxic to animals and humans due to bioaccumulation and biomagnification, resulting in many health concerns and chronic problems.

Health Concerns and Problems Associated with Heavy Metals:

According to the American Heart Association, 24.8 million men and 21.1 million women in the United States smoke cigarettes [7]. Interestingly, cigarettes contain over 4000 chemical compounds, including 433 known carcinogens, which are commonly linked to many types of cancers and other health issues [8]. Moreover, recent studies have found that cigarettes contain heavy metals such as cadmium, lead, nickel, copper, mercury, and zinc [9]. Cadmium, one of the main metals found in cigarettes, has been linked to many health issues such as lung cancer, renal failure, stomach irritation, bone diseases, and death [10]. In particular, cadmium poisoning

Figure 2. Heavy Metal Pollution Cycle [6]



is the main cause of Itai-itai, a bone disease first documented in Japan caused by cadmium-contaminated rice [11]. In one study, Masahiko Satoh et al. reported that renal dysfunction occurred at cadmium concentrations of 150 $\mu\text{g/g}$ wet tissue in rats [10]. In addition, studies show that rats incapable of producing sufficient levels of metallothionein in the kidneys suffer from renal dysfunction when the cadmium concentration is less than 10 $\mu\text{g/g}$ wet tissue [10]. Satoh et al. concluded that relatively low levels of exposure of cadmium through smoking could cause renal dysfunction in humans who cannot produce sufficient levels of metallothionein [10].

Exposure to low levels of lead, another heavy metal found in cigarettes, has been documented to cause many adverse health problems in humans. One of the main organs affected by lead poisoning is the brain. Some of these effects are delayed or reversed development, permanent learning disabilities, seizures, coma, and death [12]. In recent studies, researchers have found that exposure to low levels of lead can affect virtually every organ system in children [13].

Copper, another heavy metal found in cigarettes, is a vitally important trace element found in the human body. In particular, small amounts of copper must be present in the body in order to absorb iron from the intestinal tract, as well as release iron from storage sites in the liver [14]. Even though every individual must absorb copper each day via foods, water, and air, long term exposure to copper can cause irritation to mucous membranes, liver and kidney damage, decline in intelligence, as well as chronic diseases, such as Wilson's disease [15]. Even though Wilson's disease is a genetic-based disease, carriers of the gene responsible for Wilson's are more susceptible to developing this disease if they are smokers. In particular, Wilson's disease, also known as hepatolenticular degeneration, is a disorder in which copper cannot be eliminated from the body, resulting in copper accumulations that can be life-threatening. The most common

organs affected from Wilson's disease include the liver and brain [16]. Even though copper is the least harmful heavy metal, over exposure to this heavy metal can cause negative health problems, ultimately resulting in death.

Nickel, another heavy metal found in cigarettes, naturally occurs in the environment at very low levels and is an ingredient commonly used in steel. Additionally, high levels of nickel can be found in certain chocolates and fats, as well as vegetables from polluted soils [17]. Similar to copper, individuals can absorb nickel every day via foods, water, and air, however, ingesting or breathing large quantities of nickel can cause many adverse health concerns. In particular, high exposure to nickel can result in development of lung cancer, nose cancer, larynx cancer, prostate cancer, lung embolism, respiratory failure, birth defects, asthma, chronic bronchitis, allergic reactions, and heart disorders [17]. Interestingly, the International Agency for Research on Cancer (IARC) labels nickel within group 2B, signifying that nickel is potentially carcinogenic to humans [18]. Moreover, nickel is currently on the American Council of Governmental Industrial Hygienists' (ACGIH) Notice of Intended Changes in order to change the label of nickel to a category A1, a confirmed human carcinogen [18].

Even though zinc is a common metal that occurs naturally in the environment, zinc concentrations are rapidly rising due to mining, waste combustion, and steel processing [19]. This rise in zinc concentration is causing environmental problems, as well as human health problems. Although zinc is essential for human health at low concentrations, high concentrations of this heavy metal can cause stomach cramps, skin irritations, vomiting, nausea, anemia, damage to the pancreas, and arteriosclerosis, as well as disturb protein metabolism [19]. Additionally, unborn children and infants can be exposed to zinc through blood or their mother's milk, causing serious health concerns [19]. Because zinc is generally considered one of the least

toxic heavy metals, high concentrations of zinc are more of an eminent threat to the environment due to bioaccumulation and rendering phosphorus, an important biological molecule, useless in polluted areas [20].

As seen, the heavy metals studied in this project are of great concern to humans and the environment. Each heavy metal can cause different health concerns; however, at high concentrations, these metals can be toxic and ultimately result in death. Even though these metals cause adverse health problems and environmental concerns at high concentrations, in general, each toxic heavy metal causes adverse affects on nerves, hormones, digestion, and immune functions by binding to receptor sites and replacing essential nutrients throughout the body [13].

Regulation of Tobacco and Tobacco Products:

On June 22, 2009, President Barack Obama signed landmark legislation allowing the U.S. Food and Drug Administration (FDA) to regulate the manufacturing and marking of tobacco and tobacco products. Specifically, this bill, entitled the Family Smoking Prevention and Tobacco Control Act, creates a tobacco control center within the FDA, allowing the FDA to strictly control the tobacco industry by forcing tobacco companies to reveal all product ingredients and seek approval for any new tobacco products [21]. Moreover, this bill allows the FDA to change current tobacco product content in order to improve public health. In addition to regulating the manufacturing of tobacco products, the bill limits advertisements geared towards attracting young smokers and requires warning labels to cover 50 percent of the front and back of each cigarette pack. As stated in the Family Smoking Prevention and Tobacco Control Act, this new legislation's ultimate purpose is "to protect the public health by providing the Food and Drug Administration with certain authority to regulate tobacco products [21]."

Atomic Absorption Spectrometry:

Because of the new legislation allowing the FDA to monitor the tobacco industry, a method for the detection of heavy metals in cigarettes needs to be developed. Flame and graphite furnace atomic absorption (AA) spectrometry are ideal techniques for this detection due to high specificity and elemental selectivity, as well as AA spectrometry is a relatively simple operation technique. In general, AA spectrophotometers are comprised of five basic parts: an interchangeable light source, a monochromator, a flame or graphite furnace, a detector, and a signal processor [22]. In order to analyze elements in liquid samples, the sample undergoes the following three steps: desolvation, vaporization, and atomization [22]. As the name suggests, the desolvation step involves evaporating the liquid solvent, leaving the dry sample to be analyzed. In the vaporization step, the instrument heats the sample to a specific temperature in order to vaporize the solid sample into a gas. Finally, in the atomization step, the elements or compounds in the sample are broken down into free atoms. During the atomization step, the light source produces a wavelength specific for the desired element being analyzed. If the ions of the desired element are present in the sample, the ions will absorb the light emitted from the light source. The amount of light absorbed by the ions, or absorbance value, is directly related to the concentration of the desired element in solution. Within certain limits, this relationship is linearly described using the Beer-Lambert Law:

$$A = \epsilon lc,$$

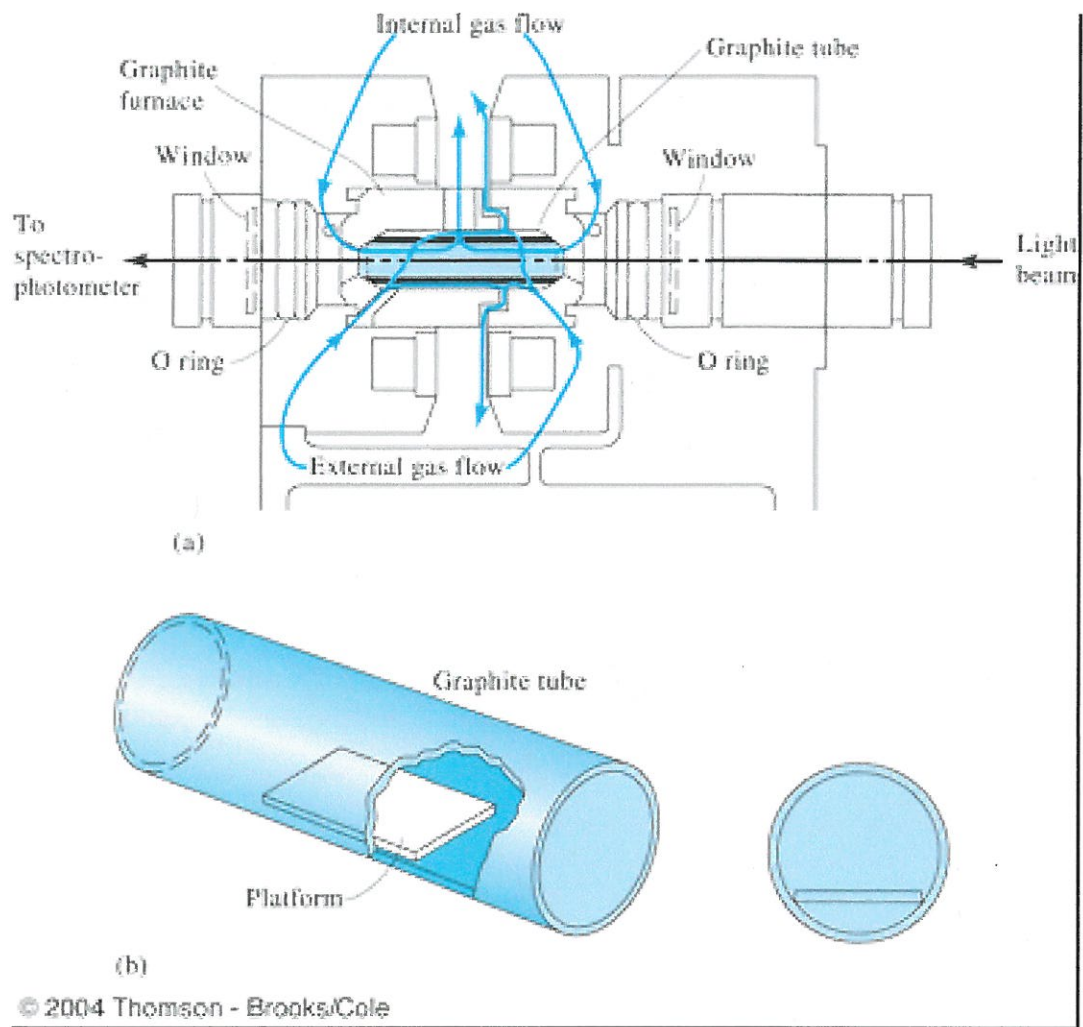
where A is the absorbance, ϵ is the molar absorptivity ($M^{-1} \text{ cm}^{-1}$), l is the path length (cm), and c is the concentration of the element in the sample (M).

As mentioned, there are two AA spectrometry methods that can be used to analyze various samples: Flame Atomic Absorption Spectrometry (FAAS) and Graphite Furnace Atomic

Absorption Spectrometry (GFAAS), also known as Electrothermal Atomic Absorption Spectrometry (EAAS). Even though both techniques utilize the same basic principles and steps, there are some notable differences between the two methods [22]. As suggested by the name, FAAS utilizes an acetylene flame to atomize the analyte. Before the sample enters the flame, it is aspirated with the acetylene gas into a nebulizer in order to form small droplets. In GFAAS, the sample is vaporized using a graphite-coated furnace instead of an acetylene flame. Figure 3 shows a schematic of a typical GFAAS instrument. As seen in this figure, argon, the external gas, flows into the tube creating an inert gas atmosphere. This inert atmosphere provides ideal conditions for atomization. Also, this figure shows the light beam traveling through the graphite tube to the spectrophotometer. Since the residence time of atoms in the absorption step is 2 to 3 orders of magnitude longer than in FAAS, the ions have more time to absorb the particular wavelength of light traveling through the furnace [22]. In addition to these differences, FAAS can only analyze solutions, whereas GFAAS can analyze solutions, slurries, and solid samples. Because very small concentrations of heavy metals (ppb) were analyzed in this work, GFAAS was employed due to its higher sensitivity, less injection volume required for analysis, inert gas atmosphere, longer residence time in the absorption step, and greater freedom from interferences [22].

In order to accurately determine the concentration of a particular element using AA spectrometry, the absorbance values can be compared to calibration curves for the particular element or the method of standard addition can be employed. Matrix effects problems can occur when the matrix, other components of the sample other than the analyte, reacts with the analyte or interferes with the response of the instrument. These matrix reactions or interferences result in an inaccurate determination of the element concentration in a particular sample. In addition to

Figure 3. Graphite Tube Utilized in GFAAS [23]



employing the method of standard addition to solve matrix effects problems, matrix modifiers should be used for Electrothermal AAS if the analyte is highly volatile or if the analyte and solvent volatilize at similar temperatures [22]. As mentioned, the method of standard addition alleviates matrix effects problems because known concentrations of the analyte are added to each sample and the data is extrapolated to determine the initial concentration of the analyte in the unknown solution. For this work, the method of standard addition was used in order to account for matrix effects and due to the low concentrations of heavy metals analyzed in the cigarettes.

Materials:

The copper, nickel, lead, and zinc standard stock solutions (1000 ppm) were purchased from Fisher Scientific (Fair Lawn, NJ). The cadmium standard stock solution (1000 ppm) was purchased from Perkin Elmer (Waltham, MA). Each stock solution was an AAS-grade standard solution. Concentrated nitric acid was from Acros Organics and reagent-grade hydrogen peroxide was purchased from Ricca Chemical.

For sonication, a VWR Scientific Products Aquasonic Model 150D was used and purchased from Fisher Scientific. A Fisher Scientific Centrifuge Model 228 was purchased from Fisher Scientific and used to centrifuge the samples. In order to analyze the heavy metal concentrations in each sample, a Perkin Elmer Analyst 800 Atomic Absorption Spectrometer equipped with an AS-800 autosampler and WinLab 32 AA Furnace Software was utilized. For each analysis, the injection volume was 5 μL .

Experimental Design:*Sample collection and pre-treatment*

Tobacco samples were collected from Camel Brand Filtered cigarettes (Batch 1DA9HP3) purchased from a local convenience store. The raw, processed tobacco was extracted from each cigarette by cutting the paper and removing the filter. Once the sample was extracted, the tobacco was ground using a mortar and pestle in order to reduce the particle size. Then, the sample was dried for 48 h in an oven at 65°C in order to remove any residual water. After removing the sample from the oven, the tobacco was re-ground using a mortar and pestle to produce a powdered sample. The sample was stored in a closed polypropylene tube at room temperature until analysis.

Ultrasound-assisted Digestion Method

Following a synthetic scheme by Kazi *et al* with minor modifications [24], we digested the tobacco samples in order to determine the concentrations of zinc, cadmium, nickel, lead, and copper using ETAAS. Since we utilized the method of standard addition, a total of eight 100 mg subsamples of dried tobacco were weighed in 50 mL polypropylene tubes. To each tube, 2 mL of a freshly prepared concentrated mixture of $\text{H}_2\text{O}_2:\text{HNO}_3$ (1:1, v/v) and 2 mL of concentrated HNO_3 were added. After leaving the samples at room temperature for 5 min, the samples were placed in an ultrasonic water bath at 80°C and subjected to ultrasonic energy for 15 min. Figure 4 is a picture describing the experimental design utilized in these experiments.

Figure 4. Experimental Design



After exposing the samples to sonication, the contents of each tube was diluted with 5 mL of millipore water and transferred to 15 mL polypropylene tubes. As seen in Figure 5, after treating the tobacco samples with H_2O_2 and HNO_3 and sonication, the reaction vessel consists of a yellowish solution and a reddish gas.

Figure 5. Reaction Vessel after Treatment and Sonication



The diluted samples were centrifuged at 3000 rpm for 15 minutes. The supernatant in each flask was transferred to a 10 mL volumetric flask and an appropriate amount of 10 ppm metal standard solution was added in order to yield the following standard concentrations: 10 ppb, 25 ppb, 50 ppb, 100 ppb, 200 ppb, 250 ppb, and 500 ppb. Following this addition, the samples were diluted to 10 mL using millipore water and transferred into 15 mL polypropylene tubes in order to store the samples at -4°C until analysis. Blanks were also treated using the

previously described method. Immediately prior to analysis, the samples were centrifuged for 15 minutes and 2 mL of the supernatant was collected in order to be analyzed using ETAAS. The concentration of each unknown sample was determined by extrapolating the standard addition curves.

Results and Discussion:

Determination of Dynamic Range:

In order to accurately determine the concentrations of various heavy metals in cigarettes, we first needed to determine the capability of the ETAAS instrument. Below are the standard curves for the following heavy metals: Cd, Zn, Cu, Ni, Pb. Each standard was prepared from a 100 ppm solution and diluted to 25 mL using millipore water. The 100 ppm solution contained all five heavy metals and was prepared from 1000 ppm stock solutions of each metal and diluted to 100 mL using millipore water. To determine the dynamic range for each heavy metal, the 100 ppm metal solution was diluted using millipore water, resulting in the following concentrations: 10 ppb, 25 ppb, 50 ppb, 100 ppb, 200 ppb, 250 ppb, and 500 ppb.

In Figure 6, the absorbance vs. concentration (ppb) data for cadmium and zinc are shown. As seen, the standard curves showed a negative correlation between absorbance values and concentration for both metals. Typically, a negative correlation is the result of matrix interference between the analyte and solvent. In other words, the solvent and analyte volatilize at similar temperatures, resulting in false positive absorbance values or false negative absorbance values. However, since the matrix in the standard solutions was millipore water, which volatilizes at 100°C, matrix interferences are an unlikely reason for the negative correlation between absorbance and concentration for cadmium, which volatilizes at 767°C, and zinc, which volatilizes at 907°C. In addition, it is unlikely that the other heavy metals in the standard solutions interfered with each other because similar results were found in the absence of the other metals. Since we could not determine the reason for the negative correlation, cadmium and zinc concentrations were not determined in the cigarette samples.

Figure 6. Absorbance vs. Concentration Plot for Cadmium and Zinc Standards

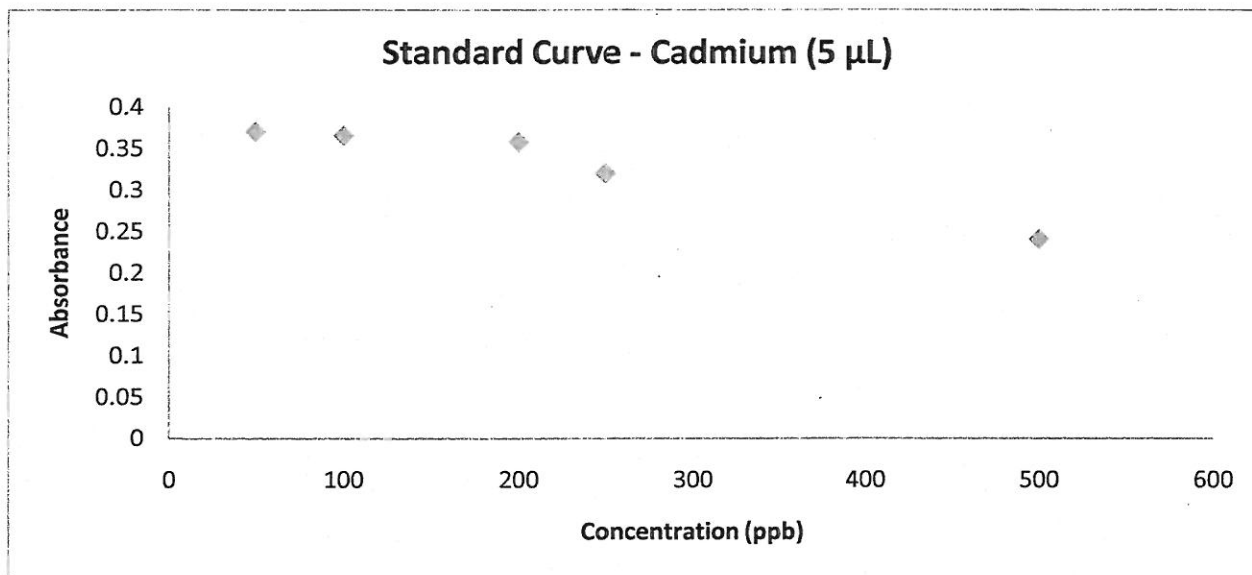


Figure 6a. Absorbance vs. Concentration Plot for Cadmium

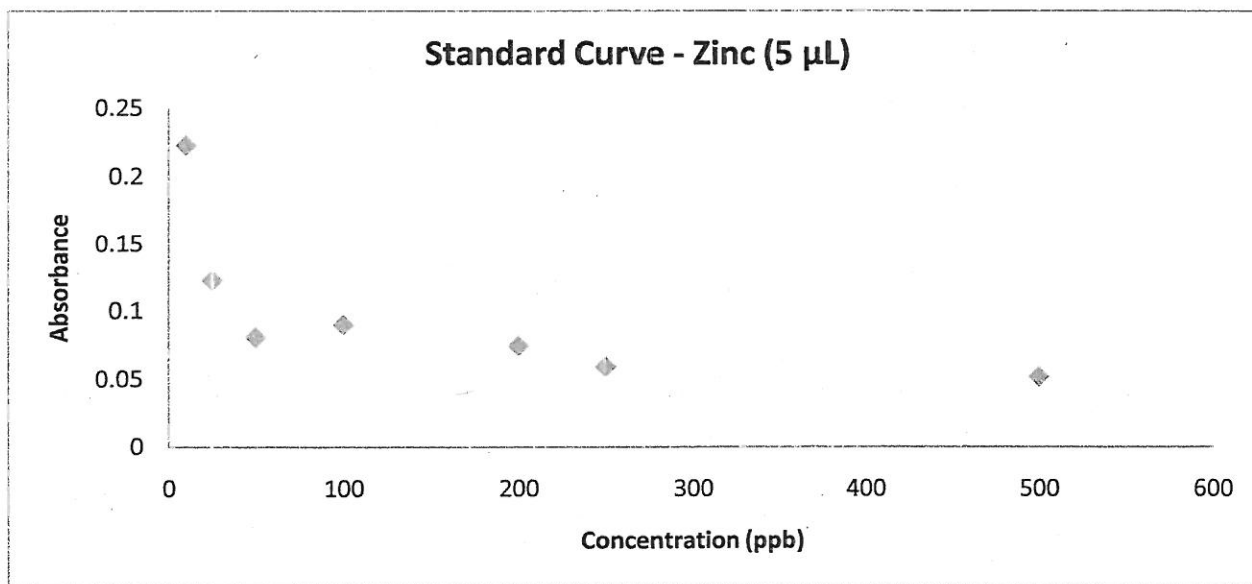


Figure 6b. Absorbance vs. Concentration Plot for Zinc

In Figure 7, the absorbance vs. concentration (ppb) plot for copper is shown. As seen, a second-order polynomial trend line with an R^2 value of 0.9756 was used due to the curvature of the data. These results indicate concentrations near or exceeding 500 ppb are too concentrated, resulting in limitations of the Beer-Lambert law. In particular, causes of nonlinearity include

interactions between molecules in close proximity due to high concentrations and alterations in the refractive index at high analyte concentrations [25]. Even though these results indicate that 500 ppb reaches the saturation point for the ETAAS, the dynamic range for copper was determined to be 10 ppb – 500 ppb.

Figure 7. Absorbance vs. Concentration Plot for Copper Standards

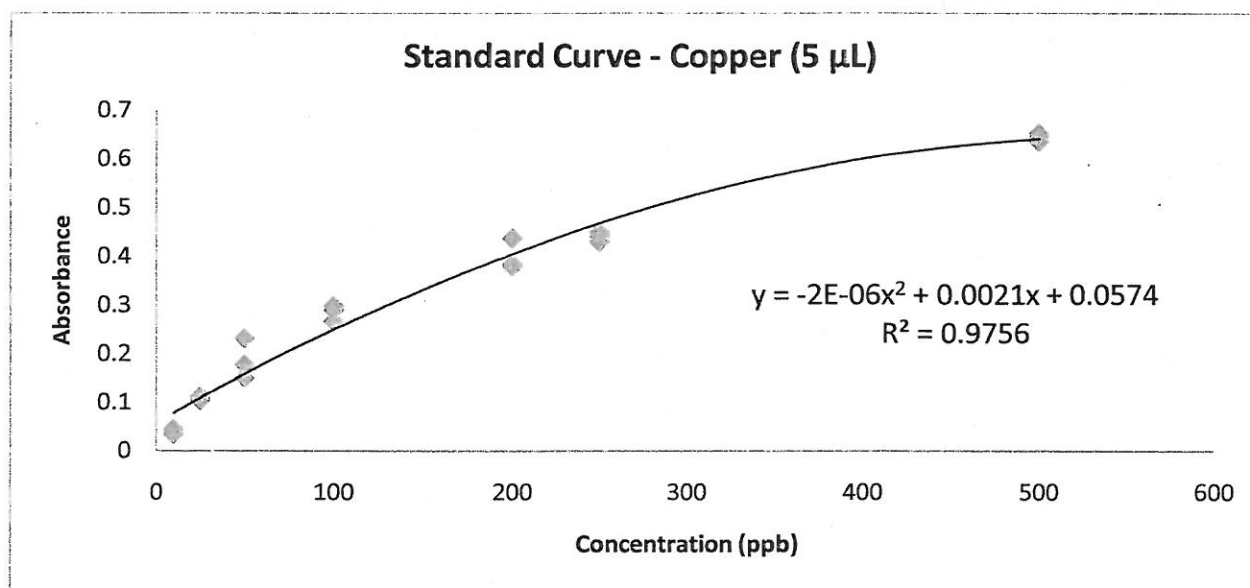


Figure 8 shows the absorbance vs. concentration (ppb) plot for the nickel standards. As seen in this plot, the data follows Beer-Lamberts Law with a R^2 value of 0.9738. The linearity of the plot indicates that there is a direct correlation between the absorbance values and concentration of the nickel standards. From these results, the dynamic range for nickel was determined to be 10 ppb – 500 ppb. Similarly, in Figure 9, the absorbance vs. concentration (ppb) for the lead standards is shown. A linear trend line with a R^2 value of 0.9873 was used to fit the data, indicating the data is consistent with Beer Lamberts Law. The dynamic range for lead was determined to be 10 ppb – 500 ppb. Due to the strong linear correlation between absorbance and concentration for both metals, nickel and lead were analyzed in the cigarette samples in order to determine the concentration of nickel and lead in an individual cigarette.

Figure 8. Absorbance vs. Concentration Plot for Nickel Standards

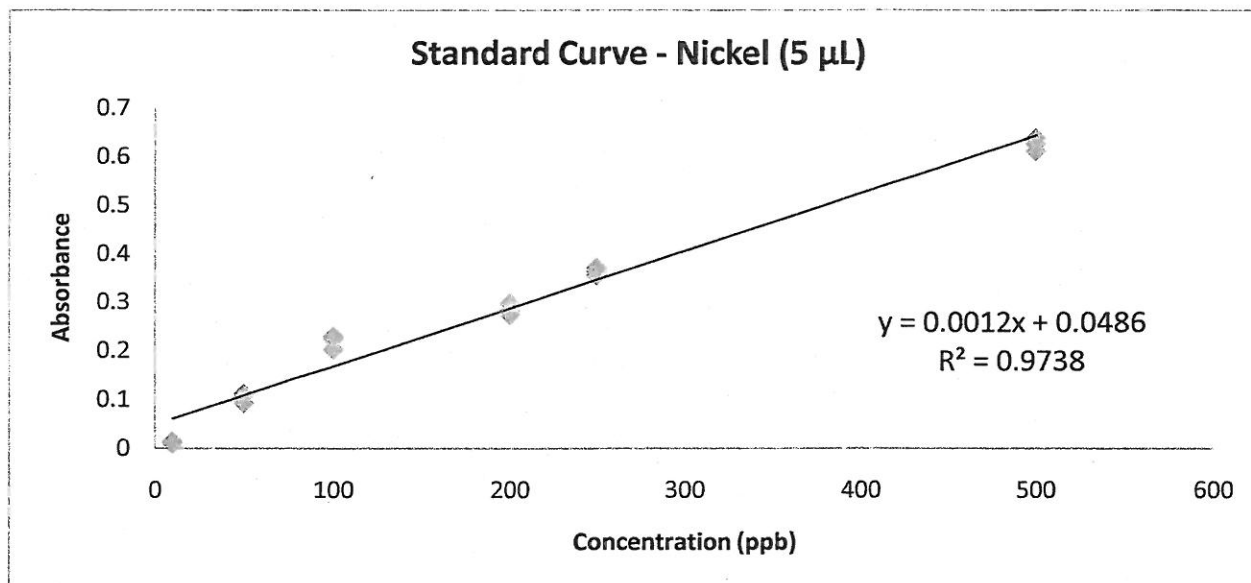
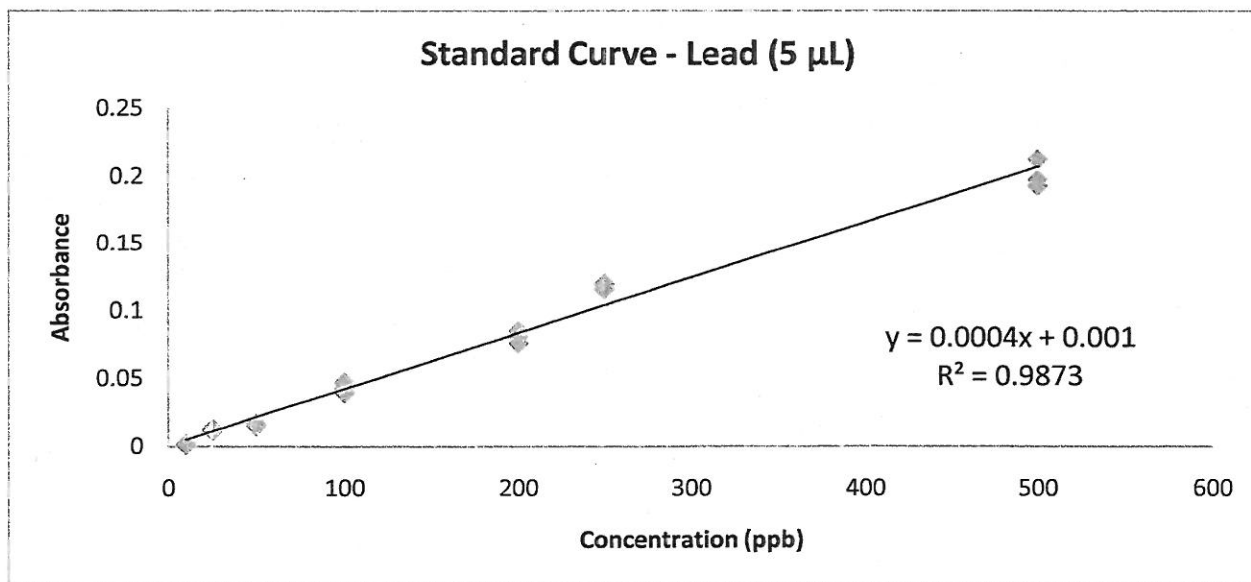


Figure 9. Absorbance vs. Concentration Plot for Lead Standards



Determination of Heavy Metal Concentrations in Cigarette Tobacco:

Based on the results from the standard curves (Figures 2-6), the concentrations of Pb, Ni, and Cu were the only heavy metals analyzed in the digested cigarette samples. As previously mentioned, the method of standard addition was used for these experiments because this method

alleviates matrix effects problems associated with complex matrices. Additionally, the method of standard addition can be utilized for analyzing low concentrations of an analyte in a sample, such as determining the concentration of heavy metals in cigarettes. In this method, known concentrations of the analyte were added to each sample and the data was extrapolated to determine the initial concentration of the analyte in the unknown solution. Below are the standard addition curves for these metals.

As seen in Figure 10, there was a linear correlation with an R^2 value of 0.83 between absorbance and concentration of standard added for lead, but the absorbance values were extremely low. Based on these low absorbance values, it is not possible to determine the actual concentration of lead in an individual cigarette. In addition, as compared to the calibration curves for lead, the absorbance values were drastically different even though the concentrations of standard added to each sample were the same concentrations analyzed for the calibration curves. After analyzing this data, we determined that matrix interactions could be a reason for the low absorbance values. In order to remedy this problem, a matrix modifier, such as ammonium nitrate or magnesium nitrate, could be added to each sample; however, due to time restrictions, this hypothesis could not be further tested.

In Figure 11, the absorbance vs. concentration (ppb) plot for nickel in the digested cigarette samples is shown. As seen in this plot, there is not a significant linear correlation between the absorbance values and concentration of standard added. As compared to the calibration curve for the nickel standards, the absorbance values were significantly higher, possibly indicating that there is a high concentration of nickel found in an individual cigarette. However, since the data does not indicate a strong correlation between absorbance and concentration of standard added due to the R^2 value of 0.3705, the Beer-Lambert Law cannot be

applied to determine the actual concentration of nickel in a cigarette. Since matrix interactions can produce false negative absorbance results and false positive absorbance results, a reaction between the nickel analyte and matrix could be the reason behind the low correlation between absorbance and concentration of standard added. As aforementioned, matrix modifiers could be used to remedy this problem, but due to time restrictions, the samples could not be re-analyzed using a matrix modifier, such as ammonium nitrate or magnesium nitrate.

Figure 10. Absorbance vs. Concentration Plot for Lead in Digested Cigarette

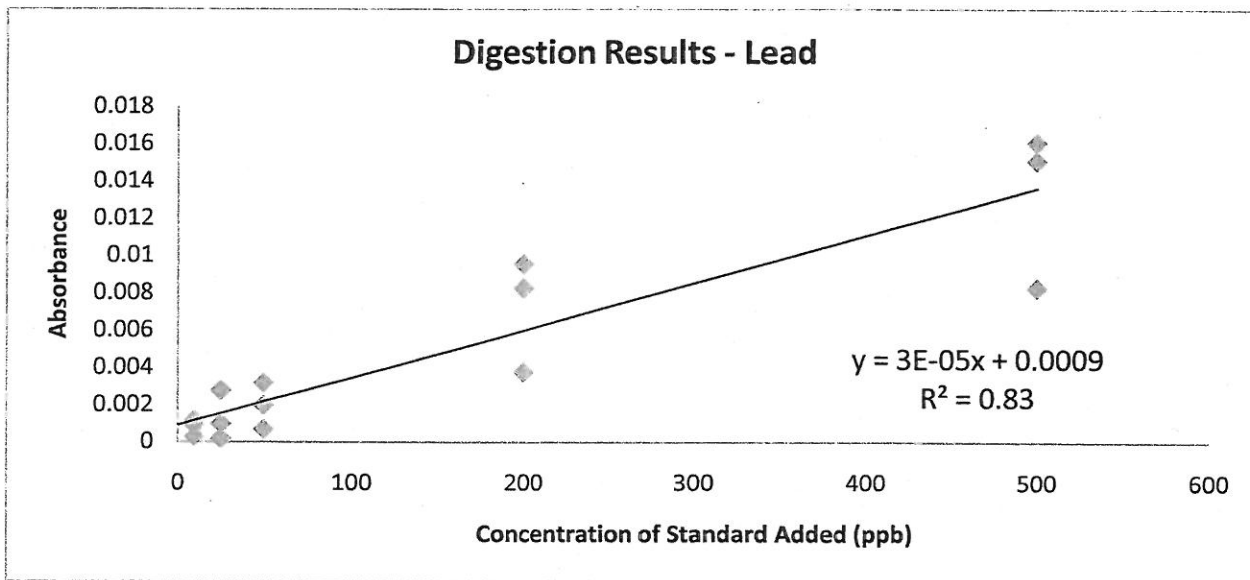
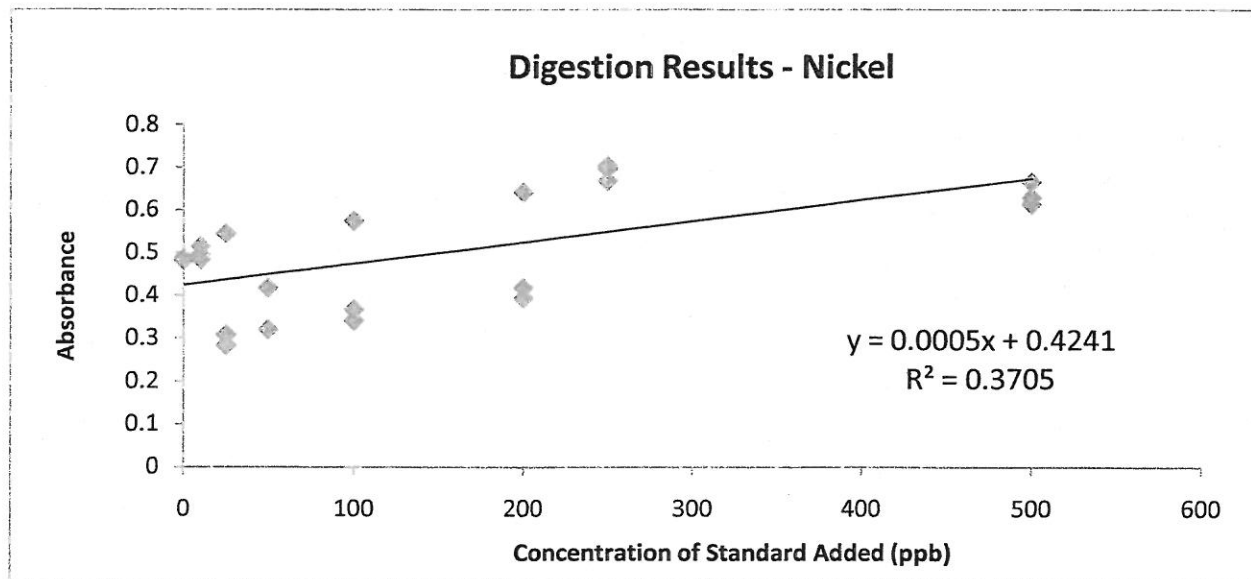


Figure 11. Absorbance vs. Concentration Plot for Lead in Digested Cigarette



In Figure 12, the absorbance vs. concentration of standard added (ppb) plot for copper in the digested cigarette samples is shown. As seen in this plot, there is a linear correlation between the absorbance and concentration of standard added for copper with a R^2 value of 0.9871. Since this data follows Beer-Lamberts Law, we can determine the concentration of copper in an individual cigarette. To determine the concentration of copper, we utilized the equation of the linear trend line, $y = 0.0011x + 0.1720$, to in order to extrapolate the data to find the concentration of copper in the unknown sample. Given that we analyzed each sample in triplicate, the concentration of copper was determined for each replicate using the equation of the trend line. The calculated concentrations of copper for each replicate can be seen in Table 1. The calculated concentrations of copper were $167 \text{ ppb} \pm 7 \text{ ppb}$, $172 \text{ ppb} \pm 2 \text{ ppb}$, and $166 \text{ ppb} \pm 2 \text{ ppb}$, which is equivalent to $16.7 \text{ } \mu\text{g/g} \pm 0.7 \text{ } \mu\text{g/g}$ sample, $17.2 \text{ } \mu\text{g/g} \pm 0.2 \text{ } \mu\text{g/g}$ sample, and $16.6 \text{ } \mu\text{g/g} \pm 0.2 \text{ } \mu\text{g/g}$ sample. Based on the data from these three replicates, the concentration of copper in a 100 mg sample is $16.7 \text{ } \mu\text{g/g} \pm 0.6 \text{ } \mu\text{g/g}$. In order to determine the concentration of copper in each cigarette, the concentration of copper per sample (in $\mu\text{g/g}$ sample) was multiplied

by the average weight of the tobacco found in a single cigarette, 0.694 g. From these calculations, the concentration of copper per cigarette for each replicate was calculated to be $11.6 \mu\text{g}/\text{cig} \pm 0.5 \mu\text{g}/\text{cig}$, $11.9 \mu\text{g}/\text{cig} \pm 0.1 \mu\text{g}/\text{cig}$, and $11.5 \mu\text{g}/\text{cig} \pm 0.1 \mu\text{g}/\text{cig}$, respectively. Based on this data, the mean concentration of copper in an individual cigarette is $11.6 \mu\text{g}/\text{cig} \pm 0.2 \mu\text{g}/\text{cig}$.

Figure 12. Absorbance vs. Concentration Plot for Copper in Digested Cigarette

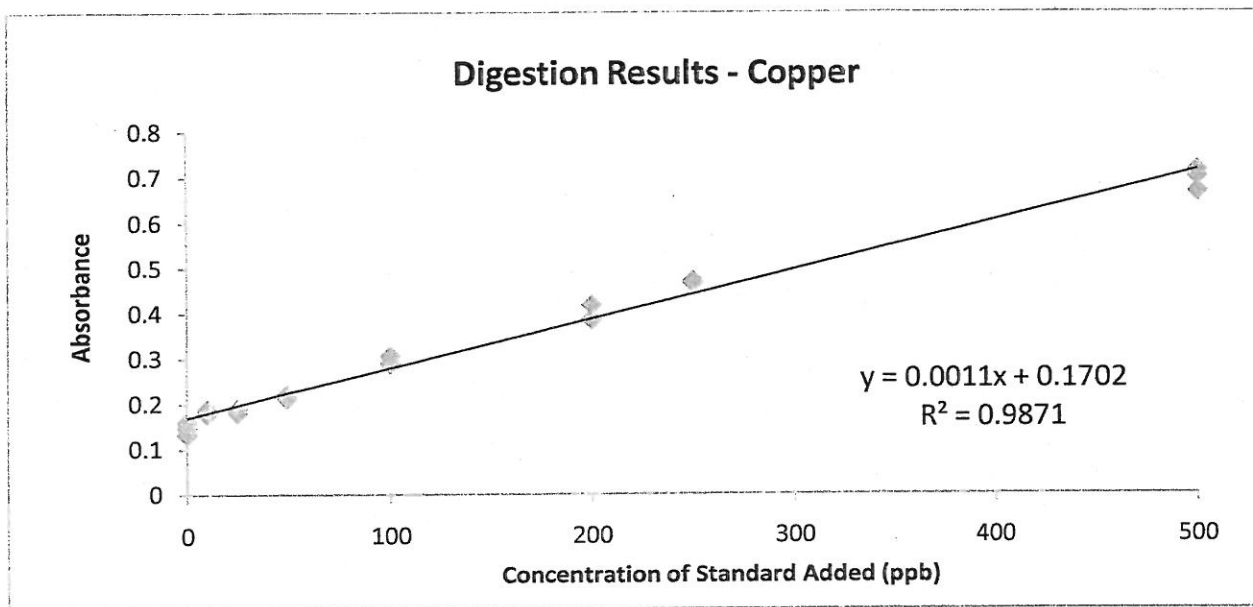


Table 1. Calculated Concentration of Copper per Sample and per Cigarette

Trial	Concentration of Copper in 100 mg sample	Concentration of Copper in Cigarette
1	$16.7 \mu\text{g}/\text{g} \pm 0.7 \mu\text{g}/\text{g}$	$11.6 \mu\text{g}/\text{cig} \pm 0.5 \mu\text{g}/\text{cig}$
2	$17.2 \mu\text{g}/\text{g} \pm 0.2 \mu\text{g}/\text{g}$	$11.9 \mu\text{g}/\text{cig} \pm 0.1 \mu\text{g}/\text{cig}$
3	$16.6 \mu\text{g}/\text{g} \pm 0.2 \mu\text{g}/\text{g}$	$11.5 \mu\text{g}/\text{cig} \pm 0.1 \mu\text{g}/\text{cig}$

Conclusions:

Ultimately, the aim of this project was to determine the effects of cigarette smoking and if direct “ashing” on the ground in a confined area resulted in negative effects on the environment. Even though this question was not directly answered in this work, great strides were made to understand the Electrothermal Atomic Absorption Spectrometer, to determine an effective method to digest cigarettes for analysis, and to determine the concentration of heavy metals in cigarettes. In our digestion method, a mixture of hydrogen peroxide and nitric acid worked to digest the organic material in tobacco, allowing the heavy metals to dissolve in solution. To aid this process, the samples were exposed to ultrasonic energy at 80°C. The method of standard addition was utilized to determine the concentrations of lead, nickel, and copper in the unknown sample. The concentration of zinc and cadmium were not analyzed due to problems with the initial calibration curves. Due to extremely low absorbance values for lead in the digested cigarette samples and a low correlation between absorbance and concentration of standard added for nickel, the Beer-Lambert Law could not be used to determine the concentration of these heavy metals in cigarettes. Given that there was a strong correlation between absorbance and concentration of standard added for copper, the concentration of copper in the 100 mg sample was calculated to be $16.7 \mu\text{g/g} \pm 0.6 \mu\text{g/g}$ and the concentration of copper per cigarette was determined to be $11.6 \mu\text{g/cig} \pm 0.2 \mu\text{g/cig}$.

Future Works:

Since the ultimate goal of this research project is to determine the environmental effects of cigarette smoking around designated smoking areas on the Longwood University campus, there is further work to be accomplished to complete this project. In particular, we need to determine copper concentrations in different cigarette brands in order to compare levels of copper in various types of tobacco. Additionally, further research shows that the use of matrix modifiers, such ammonium nitrate (NH_4NO_3) and magnesium nitrate ($\text{Mg}(\text{NO}_3)_2$), enhance absorbance values by eliminating the matrix without affecting the analyte. Since the heavy metals being analyzed and the matrix could volatilize at relatively similar temperatures, matrix modifiers could be used in order to determine the concentration of lead, nickel, cadmium, and zinc in cigarette tobacco. After determining these concentrations, ash from smoked cigarettes can be collected to determine the loss of heavy metal concentration during the smoking process. Ultimately, soil samples can be collected from smoking huts around Longwood University's campus in order to determine the concentrations of copper, lead, nickel, cadmium, and zinc in the soil and assess the effects of these smoking huts on the environment.

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