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A Novel Method for Confirming the Presence of Volatile Reduced Sulfide Compounds via Inductively Coupled Plasma-Optical Emission Spectroscopy

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A NOVEL METHOD FOR CONFIRMING THE PRESENCE OF VOLATILE

REDUCED SULFIDE COMPOUNDS VIA INDUCTIVELY COUPLED

PLASMA-OPTICAL EMISSION SPECTROSCOPY

by

Krystal Lynne Parker

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ABSTRACT

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Millions of dollars in destruction in the past decade have resulted from the use of Chinese drywall in homes. There are also potential health hazards related to this corrosive material. As such, it is important to find a way to identify Chinese drywall. Drywall can be tested for certain markers, such as strontium, sulfur, and carbonates to identify it as corrosive Chinese drywall. The laboratory preparation and analysis should be efficient and cost effective. The methods previously used, such as an X-ray fluorescence gun have had issues with getting a proper reading due to the layers of other materials found on the drywall, and instruments such as atomic absorption can only test for one metal at a time.

This investigation is beneficial because it uses a novel technique. This experiment focused on developing a method for the ICP-AES, inductively coupled plasma-atomic emission spectroscopy, which could qualitatively identify the presence of sulfide compounds in drywall. The drywall samples were set up in a natural environment, and the presence of sulfide compounds were tested for with copper coupons. The oxidized copper was then put into an acidic solution, and real time analysis was used to immediately analyze the volatilized sulfide compounds. All of the Chinese drywall samples tested positive for sulfur. This means that this type of analysis can be used to

show that drywall containing corrosive sulfide compounds can be positively identified as

Chinese drywall.

ACKNOWLEDGMENTS

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CHAPTER I

INTRODUCTION

Forensic analysis deals with both qualitative and quantitative analysis of different kinds of samples. Qualitative analysis involves specifically identifying the unknown sample while quantitative analysis allows for the determination of the concentration of the sample. Many analytical instruments can be used to test the samples, such as a gas chromatography/mass spectrometry (GC/MS), liquid chromatography/mass spectrometry (LC/MS), fourier transform infrared spectroscopy (FTIR), ultraviolet/visible spectrophotometry (UV/Vis), and high-performance liquid chromatography (HPLC). Chromatography is the most common type of analytical technique used to identify mixtures since it is capable of separating the components. When testing specific elements present in the samples, there are also various instrumentations that can be used such as an atomic absorption (AA), inductively coupled plasma-atomic emission spectroscopy (ICP-AES), and inductively coupled plasma-mass spectroscopy (ICP-MS).

Forensic analysis is a very useful tool for arson investigation and can aid in determining whether insurance fraud may have been committed. Arson investigation involves four main areas of investigation, which include proof of incendiarism, proof of opportunity, proof of motive, and miscellaneous connecting evidence (Corry, 1996). Investigating proof of incendiarism requires the examination of the fire scene to determine cause and origin. Investigating proof of opportunity deals with looking at the security of the building when the fire occurred and who had access to it. Investigating proof of motive involves looking at the owner's financial condition, cash flow, and even the profit or loss from operations. Examining connecting evidence looks at proof such as

the owner's insurance history, how well the fire and burglar detection systems were working, and even how the owner learned about the fire (Corry, 1996). Arson is one of the most common problems the insurance industry must face. The intentional destruction of property for insurance gain has been prevalent in the field of insurance since it began. Insurance fraud happens when an individual purposefully lies in order to get some sort of benefit or advantage to which they should not, or when someone denies a benefit to someone who deserves it ("What is Insurance Fraud?," 2014). Fire and other damages to property compose a large portion of insurance fraud, but it also includes other types of fraud that deal with automobile collision, medical, life, automobile property, and healthcare ("What is Insurance Fraud?," 2014).

Drywall that was causing problems in homes was linked to drywall imported from the People's Republic of China, commonly referred to as "Chinese Drywall" (Allen et al., 2012). Chinese drywall was mainly imported into the states from 2004 to 2006. However, it has been found in homes that were either built or remodeled between 2001 and 2009. Its use has been reported in 42 states, the District of Columbia, and even Puerto Rico (Chinese Drywall, 2014). It has affected numerous amounts of residential and commercial properties.

There are many signs in determining if one's property was built using Chinese drywall. The most common indicator is the smell of rotten eggs or the smell of ammonia coming and going. Another sign is the corrosion of the air conditioner evaporator coils, which is commonly mistaken as a Freon leak. Chinese drywall also corrodes electrical wiring, which could also lead to people shocking themselves when turning off the power (Chinese Drywall, 2014). Other signs of electrical problems, which are potential

indications of the use of Chinese drywall, include a circuit breaker needing constant resetting with no apparent reason, lights that randomly flicker, bright flashes or sparks anywhere in the electrical system, buzzing from the electrical system, and even discolored switch plates, outlet covers, and dimmer from overheating, and even a smell of burnt plastic ("How Can I Tell If My Home Has Problem Drywall?," 2014). The reason why Chinese drywall can cause all these problems and lead to possible fires is due to its high content of strontium sulfide, a material that emits corrosive gases. Its concentration in Chinese drywall can exceed 1200 parts per million ("How Can I Tell If My Home Has Problem Drywall?," 2014). These signs can be used in order to determine if one's property was built using some or all Chinese drywall. However, confirmation tests can also be used. Some of these include testing whether the drywall causes a piece of copper to corrode, whether the sample effervesces after the addition of acid and even elemental analysis of sulfur concentration.

For elemental analysis of drywall, one can use an inductively coupled plasma-atomic emission spectroscopy (ICP-AES) or inductively coupled plasma-mass spectroscopy (ICP-MS). Atomic emission spectrometry converts the components of the sample into atoms. During this process some of the atoms are excited to higher electronic states. As the excited atoms relax back to lower states, ultraviolet and visible line spectra are used for quantitative and qualitative elemental analysis (Skoog, Holler, & Crouch, 2007). The most common and important source for AES is a plasma source, an electrically conducting gaseous mixture that contains a high amount of cations and electrons. The most frequently used plasma source is argon plasma. With this type of

source argon ions and electrons are the conducting species, but cations from the sample can be present in small amounts (Skoog et al., 2007).

The AES ion source is also known as a torch. It contains three concentric quartz tubes where the argon gas flows through. Surrounding the tube is a water-cooled induction coil. Ionization of the flowing argon is started by a spark from a Tesla coil. The induction coil then creates a fluctuating magnetic field that interacts with the ions from the spark. All of this creates the heating of the plasma. Typically, the torch is rotated 90 degrees, so it can be axially aligned with the spectrometer system (Skoog et al., 2007). Inductively coupled plasma spectrometers can also have a torch that is radially aligned or perpendicular to its axis. The radiation emitted from the plasma is what is used for analysis. They could also have a computer that can switch back and forth between the two (Skoog et al., 2007).

There are many advantages to using this type of instrument such as the higher temperatures creating a lower susceptibility to chemical interferences. Spectra for dozens of elements can be recorded at the same time, and the spectra results for most of the elements can occur under a single set of excitation conditions. Another advantage of using the plasma source includes its ability to determine low concentrations of elements that most often form refractory compounds. Refractory compounds are compounds that are "highly resistant to thermal decomposition, such as oxides of boron, phosphorous, tungsten, uranium, zirconium, and niobium" (Skoog et al., 2007, p. 254). Plasma sources also allow the determination of nonmetals, such as bromine, chlorine, sulfur, and iodine. Other advantages include the fact that the atomization occurs in a chemically inert environment, so the lifetime of the analyte is enhanced since oxide formation is

prevented. The temperature of the plasma is also uniform, so self-absorption and self-reversal effects do not happen as often (Skoog et al., 2007). This means calibration curves are more often linear.

On the other hand, there are some disadvantages to using this method. For example, the cool plasma tail has to be removed from the light path in order to prevent interferences from oxides. Additionally, it is more difficult to prevent contaminant and thermal degradation when the torch is arranged in axial configuration.

Plasma sources produce spectra that can be used for both qualitative and quantitative elemental *analysis*. The higher quality of results comes from high stability, low background, low noise, and freedom from interferences when operated properly (Skoog et al., 2007). ICP-AES is mostly used for samples that are dissolved in aqueous or organic liquids. This type of source can analyze all metallic elements. However, the analysis of alkali metals is limited, so plasma emission is usually limited to the determination of about 60 elements.

The inductively coupled plasma-mass spectrometry (ICP-MS) can sometimes be more useful for analysis when compared to the ICP-AES. It has a low detection limit for most elements, it is very precise and accurate, and has a high degree of selectivity. An important part of the instrument is the interface that coincides with the plasma torch. This instrument can determine more than 90% of the elements on the periodic table (Skoog et al., 2007). In addition, use of a mass spectrometer has many advantages including the production of results that are simpler and easier to interpret. Something known as a matrix effect is very noticeable when elements are present in high concentrations. An easy solution to this problem would be to dilute the solutions, alter the sample

introduction procedure, or separate out the elements with high concentrations. This effect can also be eliminated with the use of an internal standard (Skoog et al., 2007). The axial arrangement is more advantageous for ICP-MS. There are some advantages to having the torch in an axial arrangement over the radial form, such as increased radiation intensity that comes from the path length being longer and even higher precision, which creates lower detection limits. The ICP-MS can be used for qualitative, semiqualitative, and quantitative analyses of elements.

Qualitation of both copper and sulfur can be used to determine if the drywall samples are regular drywall or Chinese drywall. In order to do this, instruments that analyze the elemental composition of a sample must be used. ICP-OES, graphite furnace atomic absorption spectroscopy (GFAAS), ICP-AES, and ICP-MS are some of the analytical instruments that are capable of this. This study focused on using the ICP-AES, specifically, to qualitate those specific elements and for method development for better results. The purpose of this experiment is to determine if a better method can be created for positively identifying drywall as Chinese drywall. This type of drywall is very corrosive and not only causes safety hazards for a home, but also health hazards for its inhabitants. If this investigation yields significant results, it will lend great contributions to the literature for its use of a novel technique and instrument for determining the presence of sulfide compounds in drywall.

CHAPTER II

REVIEW OF RELATED LITERATURE

Effects of Using Chinese Drywall

Chinese drywall has become a nuisance to many homeowners for almost the past 15 years. It was mainly imported and installed between 2001 and 2009, but the harmful effects are still being discovered today. So much of it was imported due to multiple post-hurricane reconstruction projects between 2004 and 2008 (Hadhazy, 2009). Recent natural disasters such as Hurricane Katrina and Rita caused severe flooding, which damaged more than 1.2 million homes. The building boom caused domestic drywall supplies to run short, so contractors used about 550 million pounds of Chinese drywall in as many as 300,000 homes nationwide (Padgett, 2009). The drywall was shipped to multiple states around the country, including 60 million pounds to Louisiana and 27 million pounds to Mississippi. Problems with housing projects built or renovated with Chinese drywall have been reported in Arizona, Alabama, South Carolina, California, Kentucky, Mississippi, Nevada, Missouri, Georgia, Ohio, Virginia, Texas, New York, Tennessee, Wisconsin, Washington, Wyoming, and Washington D.C. (Petrisor & Kanner, 2010). As of 2012, there have been over 3900 incident reports found in 43 states including the District of Columbia, Puerto Rico, and American Samoa (Allen et al., 2012).

Chinese drywall is composed of gypsum, which is calcium sulfate with two water molecules. There are two main sources of gypsum, natural minerals and synthetic materials such as fly ash. Chinese drywall seems to contain more organic material than other non-corrosive drywall. Along with containing various trace elements, it also contains large amounts of sulfur and strontium. One Environmental Protection Agency

(EPA) study determined that it contained 10 times the amount of strontium found in American drywall (Ichniowski, 2009). It contains about the same levels of iron as American drywall; however, the type of iron has not been determined. Two organic compounds, possibly associated with the acrylic paint, were also found in Chinese drywall, but not in American drywall. The concentrations of all of the organic compounds also seem to be higher in Chinese drywall when compared to American drywall (U.S. EPA, 2009). A study conducted by the EPA determined that hydrogen sulfide (H_2S), carbonyl sulfide (COS), and carbon disulfide (CS_2) gases could be produced under dry conditions; however, the last two gases increased significantly when the drywall got wet. H_2S produced higher concentrations under dry conditions versus wet conditions. According to other studies, Chinese drywall also contains iron disulfide, pyrite (FeS_2), which should never be used in building materials since the sulfide oxidation to sulfate can discolor and destroy the drywall (EMSL Analytical, Inc., 2009; Rosen, 2009). This can lead to the collapsing of the drywall material, such as those used in ceilings. Chinese drywall has also been found to contain sulfur-based fungicides used to prevent mold and the growth of bacteria while shipping the material. Chinese drywall even seems to have structural and physical differences when compared to American drywall. These differences include smaller air-void sizes and lower fiber content. This means the drywall would have a higher density, and the mechanical strength could be potentially reduced (Rosen, 2009).

Chinese drywall ended up causing many issues for homeowners. The main issues dealt with off-gassing of volatile sulfur compounds and other irritating and corrosive gases into the indoor air, which can be heightened by high temperatures and humidity.

These compounds included hydrogen sulfide (H_2S), carbon disulfide (CS_2), carbonyl sulfide (COS), and sulfur dioxide (SO_2). These gases do not only pose a potential health risk to inhabitants, but also corrode electrical and plumbing components (Petrisor & Kanner, 2010). This means electronic systems could potentially malfunction, along with air conditioning systems. Existing data does not suggests that H_2S poses a health hazard; however, it has a very unpleasant rotten-egg smell. The drywall has many other environmental effects as well. It can tarnish silverware, corrode and blacken copper pipes and wiring, cause black soot to deposit on wiring behind light switches and on washer and dryer plugs, corrode coils in air-conditioning systems, cause power outages, cause dishwashers and refrigerators to stop working, break microwave ovens, and cause lights to dim or flicker (Petrisor & Kanner, 2010). Other than the physical damage done to the home, there is also potential physical damage towards the inhabitants. The health risks include itchy and irritated skin and eyes, problems breathing, chronic coughing, nosebleeds, asthma, fatigue, headaches, insomnia, dizziness, sore throat, respiratory infections, allergies, stomach problems, joint and muscle pain, hair loss, and even a build-up of a rubber cement-like substance in the sinuses (Petrisor & Kanner, 2010). The only solution to fixing the corrosive drywall is to remove and replace it, along with the damaged plumbing and wiring (Hadhazy, 2009). This would also mean the homeowners would have to be relocated during the entire process.

<div align="center">Legislation Involving Chinese Drywall</div>

Before 2009, as many as 60 drywall related lawsuits were filed in seven states, with the majority of the cases occurring in Florida and Louisiana (Ichniowski, 2009). As of June 2009, the U.S. Consumer Product Safety (CPSC) had received more than 460

incident reports from residents in 19 states and the District of Columbia. In May 2010, reporters investigated if anything had been done to help affected homeowners and tenants. They found that in spite of a CPSC investigation in the previous year, most of the problems were still unresolved. They also discovered that some builders and suppliers knew about the defective drywall and used it anyway. People living in Habitat for Humanity homes reported health and structural complaints, and Lowe's had increased its drywall settlement offer from $4,500 up to $100,000 per victim (Cherry & Geary, 2012). In a hearing, in Washington, D.C. in 2011, it was revealed that nearly 10,000 homes nationwide had Chinese drywall, and there was enough imported into the United States to build 100,000 homes. Lawsuits against manufacturers, suppliers, builders, and their insurance companies over the defective Chinese drywall continue to increase as more of it is found in homes. People still have questions about commercial general liability coverage and homeowners' insurance coverage (Cherry & Geary, 2012).

Many senators tried to pass legislation that would potentially help those affected by the defective Chinese drywall. For example, in 2009, United States Senators Mary L. Landrieu and Bill Nelson filed the Drywall Safety Act of 2009, which aimed at initiating a recall and putting an immediate ban on defective building supplies from China. It, however, did not do anything to compensate any victims (Petrisor & Kanner, 2010). These two senators also filed a budget amendment seeking $2 million in emergency funding for Chinese drywall testing. This request did fail to move forward in the U.S. Senate. Senators Sheldon Whitehouse, Jeff Sessions, and Dick Durbin introduced the Foreign Manufacturers Legal Accountability Act of 2009, which would make it easier to

sue foreign manufacturers in the U.S. justice system, but not automatically to collect money (Petrisor & Kanner, 2010).

The first legislation related to corrosive Chinese drywall was passed in May 2009. It was an amendment to the Mortgage Reform and Anti-Predatory Lending Act, which stated that the Secretary of Housing and Urban Development along with the Secretary of Treasury had to conduct a study of the effect of defective Chinese drywall on residential mortgage loan foreclosures. It also stated that a study needed to be conducted in order to determine the availability of property insurance for homes where Chinese drywall was found (Petrisor & Kanner, 2010). Later that year in September, the Louisiana Recovery Authority set aside $5 million of federal Community Development Block Grant disaster recovery money in order to help those who rebuilt their homes with defective drywall (Petrisor & Kanner, 2010). In 2010, homeowners were able to get some relief if their homes had defective drywall that was imported between 2001 and 2009. The relief, coming from the IRS, included treating the damage from the corrosive drywall as a deductible casualty loss (Chinese Drywall Relief, 2010).

Many homeowners and tenants filed lawsuits against builders, real estate brokers, importers, exporters, and suppliers in federal courts claiming damage from Chinese drywall. As of December 2011, a preliminary settlement agreement was reached with Knauf Plasterboard, a manufacturer of the drywall used in the U.S. This settlement affects 5,200 homeowners (Cherry & Geary, 2012). This agreement creates two types of funds called the remediation fund and the loss fund. The remediation fund contains three options homeowners can use to fix their homes, including finding an approved contractor to fix their homes, choosing a contractor to improve the property, or a cash out option

where they receive a lump sum cash payment with no obligation to fix their property.

This fund also included the removal and replacement of not only the defective drywall,

but built in appliances, electrical wiring, and fire and smoke alarms. The loss fund

compensates victims for economic loss associated with the drywall, which includes short

sale or foreclosure. Victims can also seek compensation for bodily injury related to the

drywall. This agreement also allowed $160 million in attorney's fees which was separate

from the compensation (Cherry & Geary, 2012).

<div align="center">Elemental Analysis for Determining Corrosive Drywall</div>

In 2009, the CPSC along with the EPA, the Centers for Disease Control (CDC),

and the Agency for Toxic substances and Disease Registry (ATSDR) initiated a multi-

agency investigation into the thousands of drywall complaints (Allen et al., 2012). Since

then many studies have been conducted in order to determine if the drywall used in

buildings is corrosive or not. These studies not only help with the safety of the

inhabitants, but also aid in court proceedings, especially lawsuits. The majority of these

studies had the same applications which included identifying and linking "environmental

effects perceived by residents or observed through testing in homes with Chinese

drywall, identifying specific effects through reliable testing, linking the identified effects

to their specific source, and linking the Chinese drywall to the specific manufacturer"

(Petrisor & Kanner, 2010, p. 10). The purpose of the investigations was to provide

reliable and defensible sampling methods. Their aims included: investigating the

variation in batches of drywall and to what extent it relates to legal questions,

investigating what adverse health impacts are related to corrosive drywall, and

investigating effects related to defective drywall other than off-gassing and corrosion (Petrisor & Kanner, 2010).

Since corrosive drywall, also known as Chinese drywall, has become such a problem in the recent years, some researchers have created methods to determine if the drywall used is corrosive or not. Some tests are simple and can be used in the field, while others have to be done back in a laboratory. Many laboratory investigations found higher levels of elemental sulfur and higher emissions of reduced sulfur gases in homes with corrosive issues compared to homes with no complaints (Allen et al., 2012). A majority of researchers use the strontium or sulfide content as a marker for the drywall being corrosive. Most field tests are just simple visual evaluations, such as looking at nearby copper components and air conditioning coils for black soot or paying attention to any smells. However, confirmation testing has to be done in a laboratory. One study determined that the gases that are released when corrosive drywall is used are hydrogen sulfide and sulfur dioxide (Babich, Saltzman, & Thomas, 2010). In order to examine the gases released for corrosive drywall, one group of researchers used gas chromatography olfactometry and found that it contained various organic thiols (Burdack-Frietag, Mayer, & Bruer, 2009). Another study looked to "characterize the indoor environment in representative complaint homes in detail, obtain air samples and other objective measurements" (Allen et al., 2012, p. 113) in order to look at future risk assessments and link the drywall to health stressors. They found that homes with strontium concentrations greater than 1200 mg/kg and carbonate higher than 5 absorbance units were built with Chinese drywall (Allen et al., 2012).

There has not been much testing done to quantitatively determine the metals present in Chinese drywall. Environmental Health and Engineering used X-ray fluorescence (XRF), corrosion-chamber tests, and ICP to analyze 35 samples of drywall from 51 different homes (Environmental Health and Engineering, 2010). Steiner (2011) tried to do something similar by using a handheld XRF and atomic absorption (AA). The XRF allows for rapid testing and does not require every single sheet to be tested. The XRF attempted to measure the strontium content, but did have some issues if there were paper, paint, and other compounds on top of the drywall. In order to quantitatively determine the amounts of strontium in the drywall, an AA technique that was developed for analyzing cements was used (Steiner, 2011). This technique is highly sensitive and precise for measuring concentration and providing quantitative measurements of strontium. Steiner (2011) determined the AA was able to accurately measure the amount of strontium and compared the AA results to the XRF results to establish a correlation. Findings indicated a linear correlation between the values obtained by the XRF and the actual values measured by AA (Steiner, 2011). Steiner (2011) also conducted laboratory exposure tests to determine if the drywall sample was corrosive or not by placing a copper coupon in an exposure chamber along with a drywall sample. The conditions were controlled, and the samples were observed at regular time intervals. The drywall samples were considered corrosive if a black tarnish on the copper coupons appeared after five or ten days of exposure (Steiner, 2011). Due to false negative results for strontium from an XRF gun, Allen and colleagues (2012) used Fourier Transform Infrared Spectroscopy (FTIR) for their analysis. They found that the FTIR cannot determine carbonate content through the paint and plaster on the drywall, so a combination of XRF and FTIR was

used on a core sample of drywall to look and strontium and carbonate content (Allen et al., 2012).

CHAPTER III

METHODOLOGY

Preliminary Procedures

In a previous study, conducted by Bonner Analytical Testing Company, eighty Chinese drywall samples were collected from fifty multi-family apartment complexes on the coast of Mississippi. The homes were rebuilt after being destroyed from Hurricane Katrina. The drywall samples were collected and tested due to the rising issues with mold and corroded appliances in the re-constructed buildings. Each sample was weighed out between 10-15 g. The samples were set up in a natural environment using deionized water, an absorbent cloth, and a copper coupon. One of the samples was digested with various reagents, such as nitric acid (HNO_3), hydrochloric acid (HCl), and hydrogen peroxide (H_2O_2). Both the digested sample and the oxidized copper from the samples in the natural environment set up were analyzed via ICP-AES. Based on the results of the preliminary IECs, inter elemental correction factors, and MDL, minimum detection limit, studies and the initial trial runs, a final method was developed and used to analyze the drywall samples. Depending on the results of the method below, a different method was developed and tested in order to possibly obtain better results.

Preparation of 1:1 Nitric Acid

The 1:1 nitric acid solution used when digesting the samples was made with both concentrated nitric acid and distilled water using the following steps:

1. 500 milliliters of distilled water was added to a 1000 mL beaker.

2. 500 milliliters of concentrated nitric acid was added to the same 1000 mL beaker.

Preparation of 1:1 Hydrochloric Acid

The 1:1 hydrochloric acid solution that used when digesting the samples was made with concentrated hydrochloric acid and distilled water with the following steps:

1. 500 milliliters of distilled water will be added to a 1000 mL beaker.

2. 500 milliliters of concentrated hydrochloric acid will be added to the same 1000 mL beaker.

Preparation of Acidified Water

The acidified water solution that was used during the real time analysis of the samples was made with concentrated nitric acid, concentrated hydrochloric acid, and distilled water with the following steps:

1. 940 milliliters of distilled water was added to a 1000 mL beaker.

2. 10 milliliters of concentrated nitric acid was added to the same 1000 mL beaker.

3. 50 milliliters of concentrated hydrochloric acid was added to the same 1000 mL beaker.

Preparation of Metal Standards

Purchased standards of metal mixtures were used in order to prepare standards for the eight-point calibration curve. The calibration curve had a linear range of 20 ppm. Table 1 shows the different elements tested in the samples.

Table 1

Metals with Respective Wavelengths

Element	Wavelength (nm)
Al	396.1
Ca	318.1
Co	228.6
Cr	267.7

Table 1 (continued).

Element	Wavelength (nm)
Cu	224.7
Fe	259.8
Li	670.7
Mg	279.0
Mo	202.0
Ni	231.6
Pb	220.3
S	182.0
Sb	206.8

Demonstration of Project

The Chinese drywall samples were prepared for testing in a natural environment through the following steps:

1. 25 mL of distilled water along with an absorbent cloth was added to a 100 mL digestion tube.

2. 10-15 g of drywall was added to the same tube.

3. A hole was drilled on the top of the tube cap and a piece of copper wiring inserted.

4. The amount of time it takes the copper to oxidize was recorded.

Preparation of Drywall Samples

Acid Digestion for ICP-AES

1. 1 cm piece of copper from drywall demonstration was added to a tarred 50 mL polypropylene digestion tube.

2. 10 mL of the 1:1 HNO_3 solution was added to the tube. The tube was then covered with a reflux cap.

3. The digestion tubes were then heated in a digestion block for 15 minutes at 95±3°C.

4. After the samples were heated they were allowed to cool to room temperature. Then 5.0 mL of concentrated HNO$_3$ was added to the tube and heated again on a digestion block for 30 minutes at 95±3°C.

5. The previous step was repeated if any fumes were given off and the tube was heated for a total of 2 hours.

6. The samples were once again allowed to cool at room temperature. Then 2.0 mL of deionized water and 3.0 mL of 30% H$_2$O$_2$ were added to the tube. It was then heated for an additional 2 hours at 95±3°C.

7. The samples were then allowed to cool at room temperature and 10 mL of concentrated HCl was added to the tube and heated for 15 minutes at 95±3°C.

8. The samples were then allowed to cool to room temperature and poured into a 100 mL sample tube and diluted to 100 mL with deionized water.

Preparation and Analysis of Non-digested Drywall Samples

1. 40 mL of acidified water, 1%HNO$_3$/5% HCl, was added to a 50 mL polypropylene digestion tube.

2. The autosampler straw was moved to the sample tube, and the analysis was done in real time.

3. After the first reading was done, or baseline, a piece of the copper from each of the samples from the visual demonstration was dropped into the 50 mL polypropylene digestion tube.

4. Initially 40 repetitions were done, and the results were monitored.

Calibration and Standardization Parameters

8-point calibration curve

Percent Relative Standard Deviation (%RSD) of ± 30%

Correlation Coefficient of ≥ 0.995

Initial Calibration Verification (ICV), ± 10%

Continuing Calibration Verification (CCV), ± 10%

Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB)

Inductively Coupled Plasma-Atomic Emission Spectrometry Parameters

Warm-up time: 30 minutes

Argon gas supply: 90 psi

Chiller temperature: 20°C

Spray chamber: glass cyclonic

Centre torch: 2.0 mm ID

Sample loop size: 4 mL

Sample pump tubing: 1.016 mm

Waste pump tubing: 1.524 mm

Exposure time: 30 sec

Number of repeats: 40

Sample flush time: 50 sec

PF power: 1150 W

Pump rate: 50 rpm

Auxiliary gas flow: 0.50 L/min

Nebulizer gas flow: 0.60 L/min

Coolant gas flow: 12 L/min

Purge gas flow: normal

Camera temperature: ~48°C

Optics temperature: camera temperature + 10°C ±2

Wash time inbetween samples: 50 sec

Sample run time: 30 minutes

CHAPTER IV

ANALYSIS OF DATA

Fifty of the eighty samples collected and prepared were used for this research. A sulfide standard was also obtained for comparison purposes. Regular drywall was also obtained to use as a control. Each of the fifty samples, along with five duplicates, a control, and a blank containing no drywall, were set up in a natural environment using distilled water, an absorbent cloth, and a copper coupon in a 100 mL digestion tube. This set-up took about thirty days for the sulfur to reduce to volatile sulfide compounds.

Before the drywall samples could be tested a method for analysis needed to be developed and modified. In order to do this an inter elemental correction factors (IECs) study and method detection limit (MDL) study were conducted. The following elements were looked at, in order to determine if they interfered with the 224.7 nm copper (Cu) line or 182.0 nm sulfur (S) line, aluminum, calcium, iron, magnesium, lithium, lead, molybdenum, cobalt, antimony, chromium, nickel, and tungsten. The wavelength lines for both copper and sulfur were chosen because they were both in the low axial view of the plasma torch, and the IECs study showed no interferences at those wavelengths as shown in Table 2.

Table 2

Results of IECs Study

Element (nm)	Interferences	Found Analyte (ppb)	Found IEC (ppb)	IEC Value
Aluminum (396.152)				
	Mo	86.428	2035	0.042470
Copper (219.958)				
	Al	-144.76	385010	-.000376

Table 2 (continued).

Element (nm)	Interferences	Found Analyte (ppb)	Found IEC (ppb)	IEC Value
Lead (168.215)				
	Fe	6.3982	40260	0.000159
	Li	9.2545	1989.5	0.004667
	Cu	-21.401	42452	-0.000534
	Mo	9.4887	2035	0.004680
	Co	5.6853	5430.5	0.001052
	Sb	5.1802	7971.9	0.000653
	Ni	6.2670	8528.3	0.000739
Lead (220.353)				
	Al	99.807	385010	0.000259
	Mo	12.040	2035	-0.005953
	Fe	4.1900	40260	0.000147
Antimony (206.833)				
	Cr	28.081	4236	0.006629

Then a MDL study was conducted in order to prove instrument stability. Seven samples

at concentrations near the expected limit of detection for each of the elements previously

mentioned were created and analyzed. The standard deviation of the results was

calculated and then multiplied by a one-sided t-distribution. The t-value used was for

seven samples with six degrees of freedom and a 99% confidence interval. These results

are shown in Table 3.

Table 3

Results of MDL Study

	Cu (224.7), (ppb)	S (182.0), (ppb)
MDL01	1.4238	8.3703
MDL02	1.5054	10.306
MDL03	1.3412	8.1700
MDL04	1.3555	10.735
MDL05	1.3456	11.309
MDL06	1.1974	8.2033

Table 3 (continued).

MDL07	1.2422	9.0892
Average Mean	1.344443	9.454686
Standard Deviation	0.103613	1.312014
t-test	3.143	3.143
MDL	0.325656	4.123659

The sodium sulfide standard was used to set up a similar man-made environment in order to develop and modify the method for ICP-AES analysis. A 1000 ppm sulfide standard was used to make samples in the concentrations of 500 ppm and 50 ppm. The standard was diluted with distilled water for both samples. Then a hole was drilled on the cap of the 50 mL polypropylene digestion tube, and a two and a half inch copper coupon was inserted. Then, two to four milliliters of concentrated nitric acid was added to both samples. After the addition of acid the samples were capped and sealed tight. For the 500 ppm sample, the copper oxidized within an hour. For the 50 ppm sample, the copper oxidized within twenty-four hours. These samples were then analyzed via the ICP-AES to further prove none of the elements in the IECs study interfered with copper and sulfur and that none were found except copper and sulfur as shown in Table 4. The concentration results from this experiment along with the results from the IECs and MDL study were determined using an eight point calibration curve made from a metals mixture standard. An ICV, ICB, CCV, and CCB were also run for quality control purposes. As one can see in Figures 1 and 2, the calibration curves pass the acceptance criteria for quality control measures. The quality control limits were also met as seen in Table 5.

Table 4

Analysis of Oxidized Copper with Multiple Elements Turned On

Element	Concentration (ppb)
Al	-0.69216
Ca	-3.0689
Co	-0.05575
Cr	0.0946
Cu	76.983
Fe	-1.135
Li	-0.11027
Mg	-2.3367
Mo	0.10518
Ni	0.80947
Pb (168.2 nm)	4.0209
Pb (220.3 nm)	3.1076
S	67.529
Sb	-0.06131
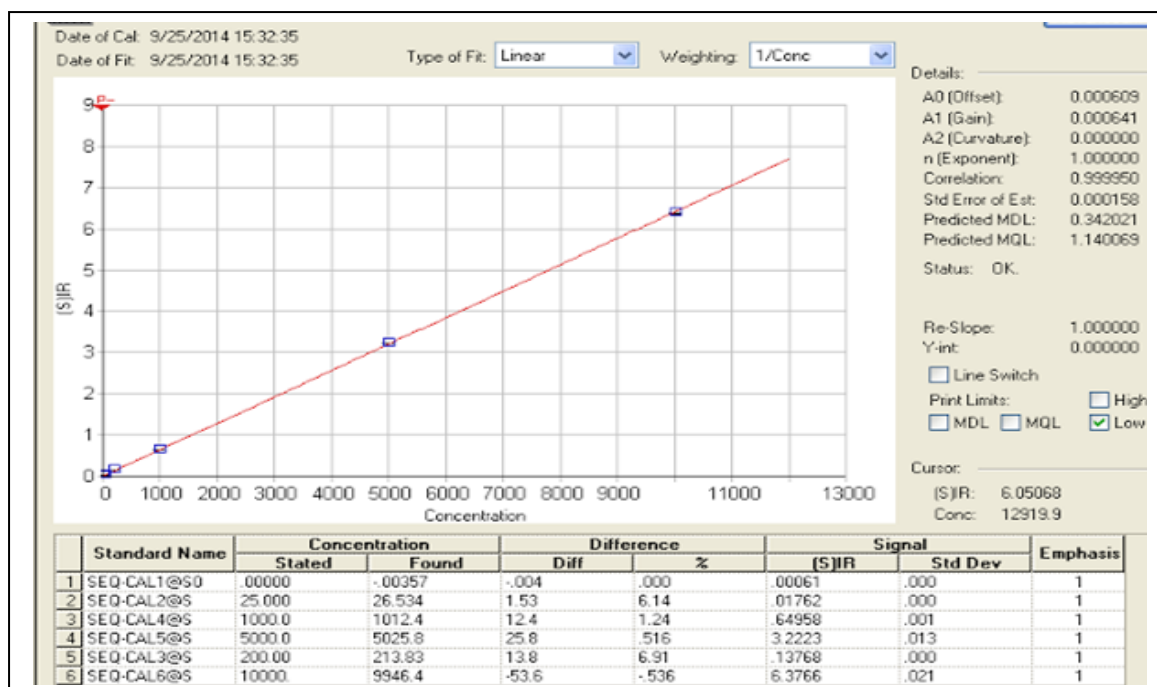
Figure 1. Calibration curve for copper. Correlation coefficient of 0.999950 and %RSD of ± 7%.
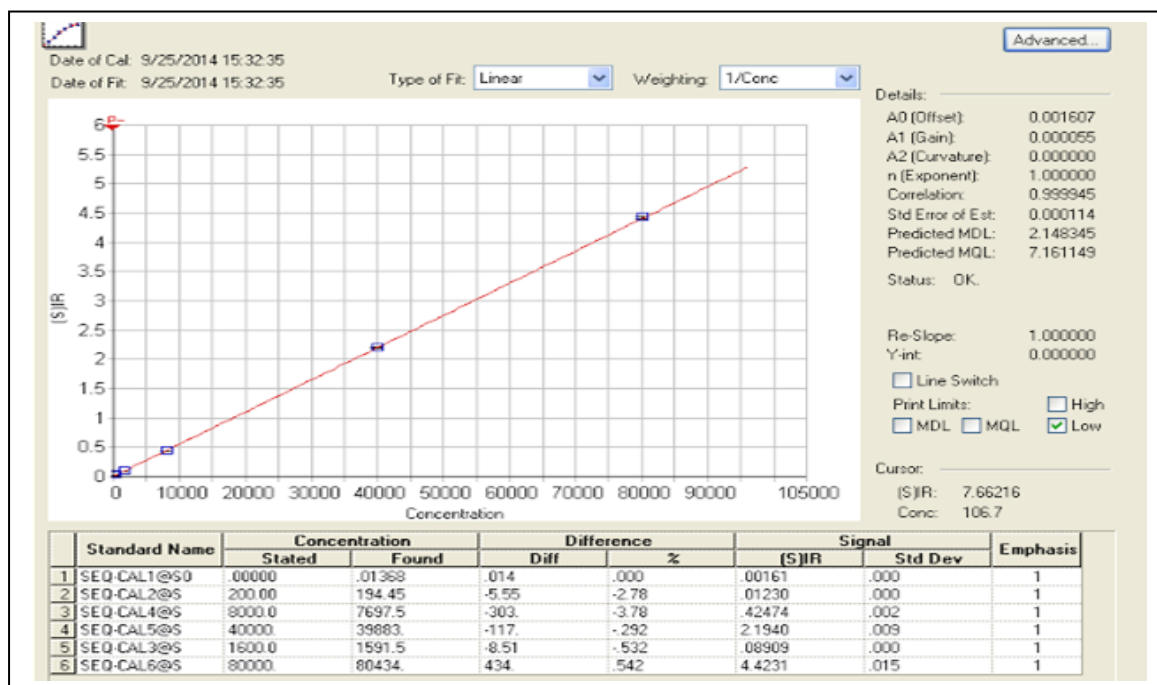

Figure 2. Calibration curve for sulfur. Correlation coefficient of 0.999945 and %RSD of ± 4%.

Table 5

ICV and CCV Results

		True (ppb)	Found (ppb)	% Difference
ICV				
	Cu	492	511.08	3.80
	S	1000	1037.4	3.41
CCV				
	Cu	5000	4858.2	-2.88
	S	40000	40335	0.834

The method was then modified to only test for copper and sulfur based on these results along with the results of the IECs and MDL studies. The samples made from the standard were also used in order to modify the method further. Once the method was switched to real time analysis, they helped determine how many replicates needed to be done and at what repeat the piece of copper needed to be dropped in at. It was determined that 40 replicates needed to be done, and the copper needed to be dropped in after the fifth replicate in order to obtain results where a baseline could be seen towards the beginning and end of analysis. The same samples were used to show that the developed method worked best when the exposure time for low axial was set at 30 seconds and set at one second for all other views including high axial, low radial, and high radial. The number of replicates along with the exposure times resulted in sound data. The results of the samples made from the sodium sulfide standard can be seen in Figure 3.
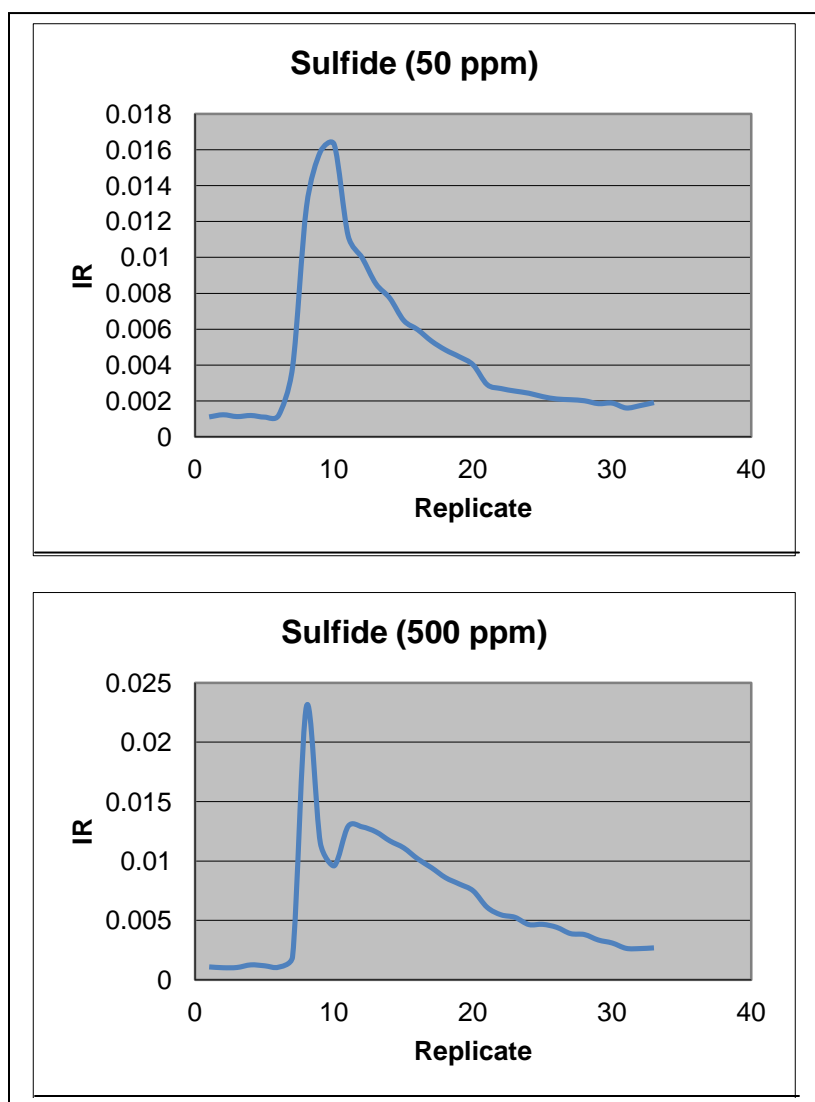
Figure 3. Analysis of the 50 ppm and 500 ppm samples. These were made from the sodium sulfide standard in order to test developed method.

The samples made from the sulfide standard were also used to show that a modified 3050B method cannot be used for analysis to positively identify if drywall is Chinese drywall or not by looking at sulfur content. The certified 3050B method uses nitric acid and hydrochloric acid in order to break down complex metals. It also uses hydrogen peroxide in order to break down complex organics. Based on previous research, these reagents would cause the gaseous sulfide compounds to volatilize. The hypothesis,

which was later proven valid, was that the sulfur would volatilize out of the sample during the digestion procedure, and only copper would be seen in the analysis. One can see that this occurred for both the 50 ppm and 500 ppm samples in Figures 4 and 5. The first graph in Figure 4 depicts an instrument response around 30 for each replicate of copper shown in blue, while the instrument response for sulfur is around zero for each replicate shown in red. The second graph in Figure 4 is just a magnification of the instrument response for sulfur at all replicates, which shows the response was between 0.0005 and 0.001. The first graph in Figure 5 depicts an instrument response around 20 for each replicate of copper shown in blue, while the instrument response for sulfur is around zero for each replicate shown in red. The second graph in Figure 5 is a magnification of the instrument response for sulfur at all replicates, which shows the response was between 0.0005 and 0.001. One can also see that since the copper was in solution due to the digestion procedure, no baseline could be obtained in both of the analyses.
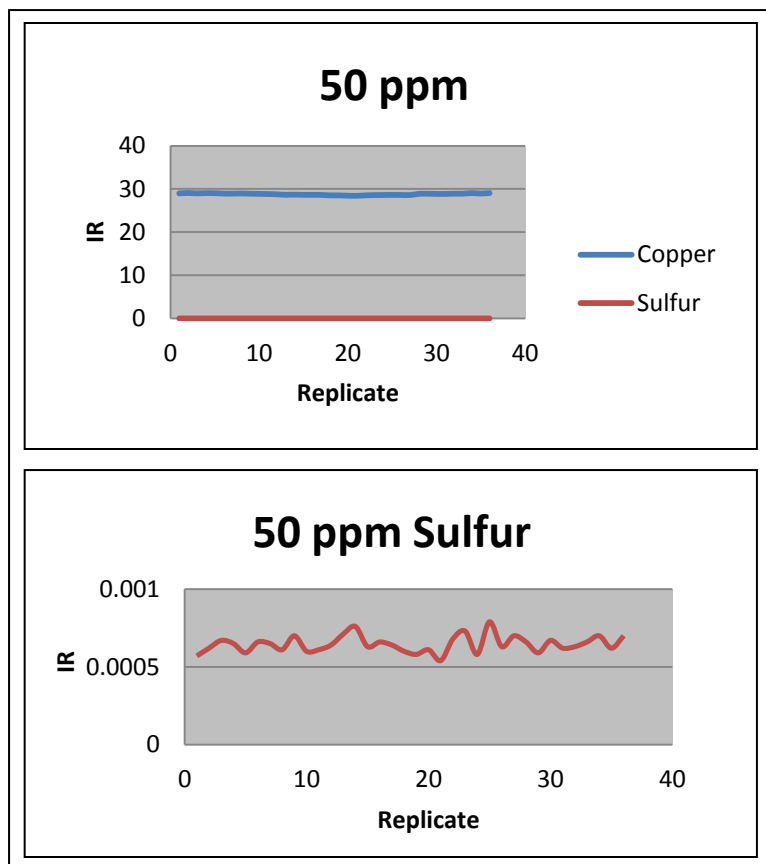
Figure 4. Analysis of the oxidized copper from sulfide standard at 50 ppm. Sulfur results were magnified in the second graph.
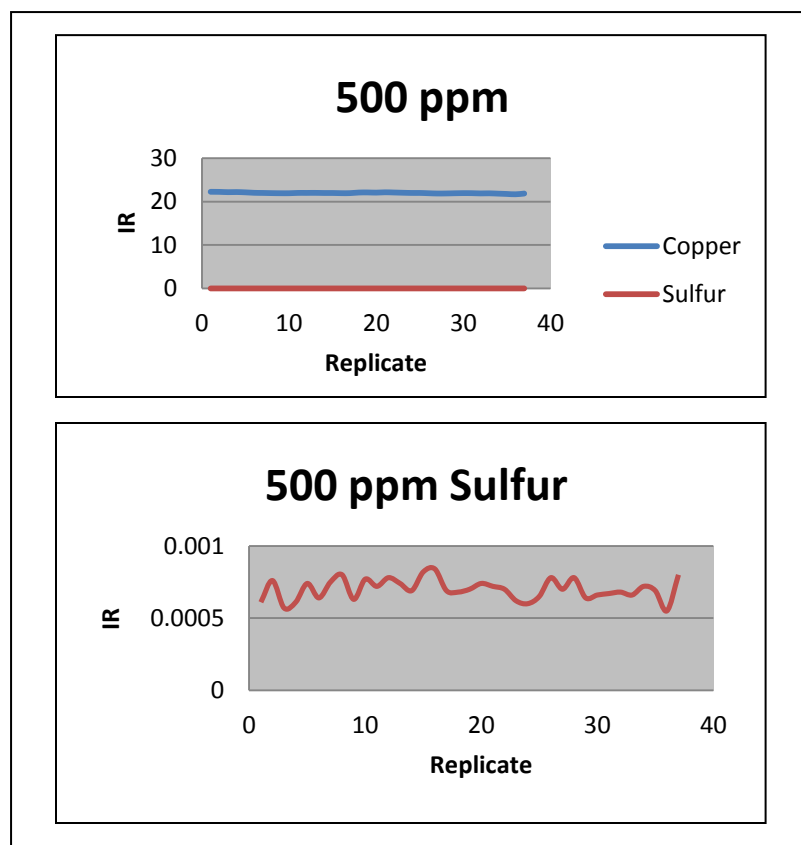
Figure 5. Analysis of the oxidized copper from sulfide standard at 500 ppm. Sulfur results were magnified in the second graph.

Once the method was finalized, real time analysis was done on the fifty Chinese drywall samples prepared in a natural environment. A blank sample of just a piece of copper was run for every twenty samples, and a duplicate was run for every ten samples to prove reproducibility. A control of just regular drywall was also analyzed. The blank and control showed no evidence of sulfur as can be seen in Figures 6 and 7. Figure 6 depicts the instrument response for all replicates for copper and sulfur in all three blanks. The results for copper for the first blank can be seen in purple, the second blank in light blue, and the third blank in orange. The results for sulfur for the first blank are in dark blue, the second blank in red, and the third blank in green. Since all three results were around zero, the second graph shows a magnification of all three sulfur results in order to show the instrument response results were between 0.001 and 0.0016. Figure 7 depicts

the instrument response for all replicates for copper and sulfur in the control sample. The results for copper can be seen in blue, while the results for sulfur are in red. The second graph is to depict the magnification of the sulfur results in order to show they were between 0.0012 and 0.0018, specifically.
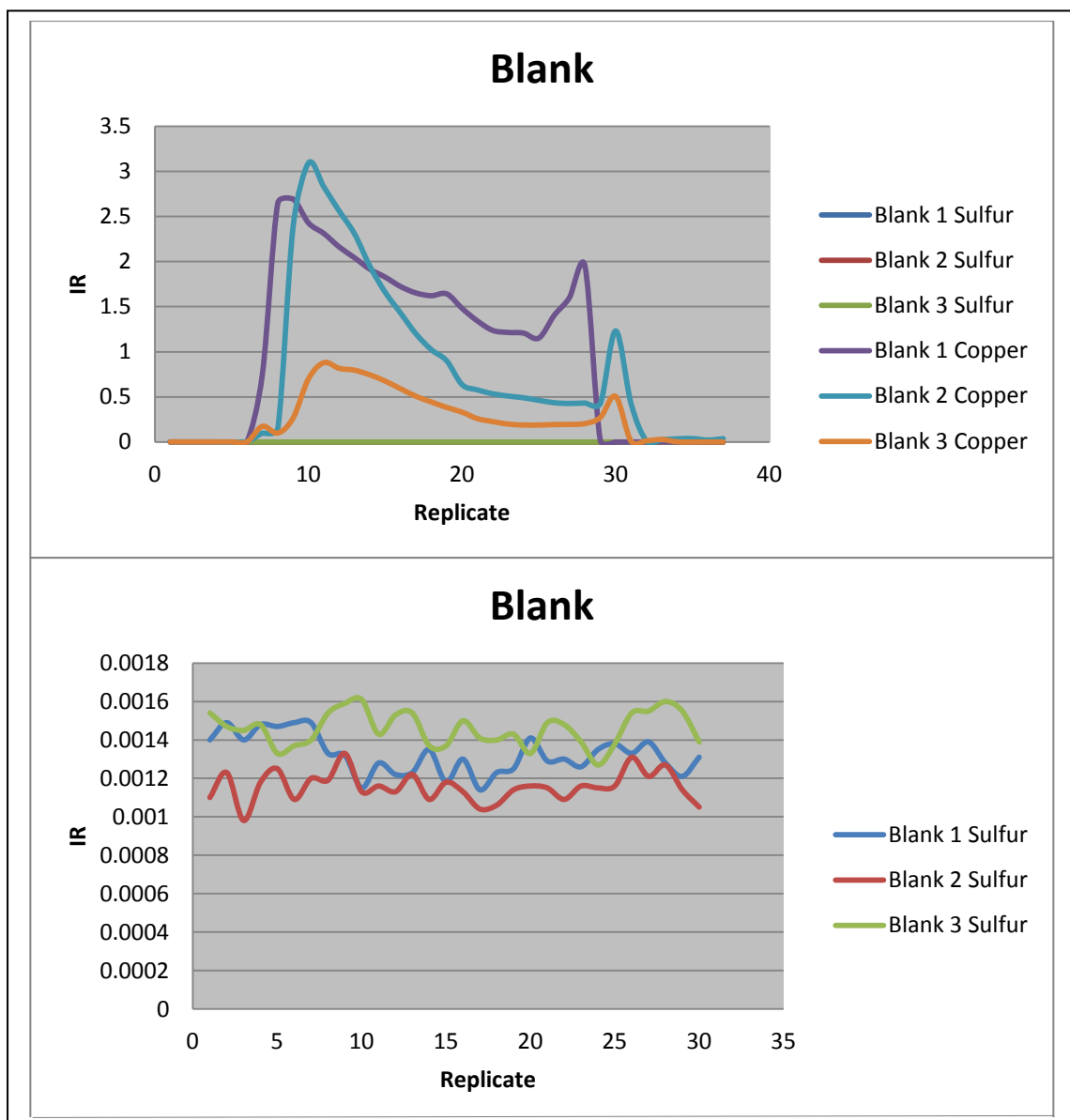

Figure 6. Real time analysis of all three blanks. Second graph shows magnification of sulfur results.

Control

(graph: IR vs Replicate, with Copper and Sulfur legend)

Control

(graph: IR vs Replicate, magnification of sulfur results)
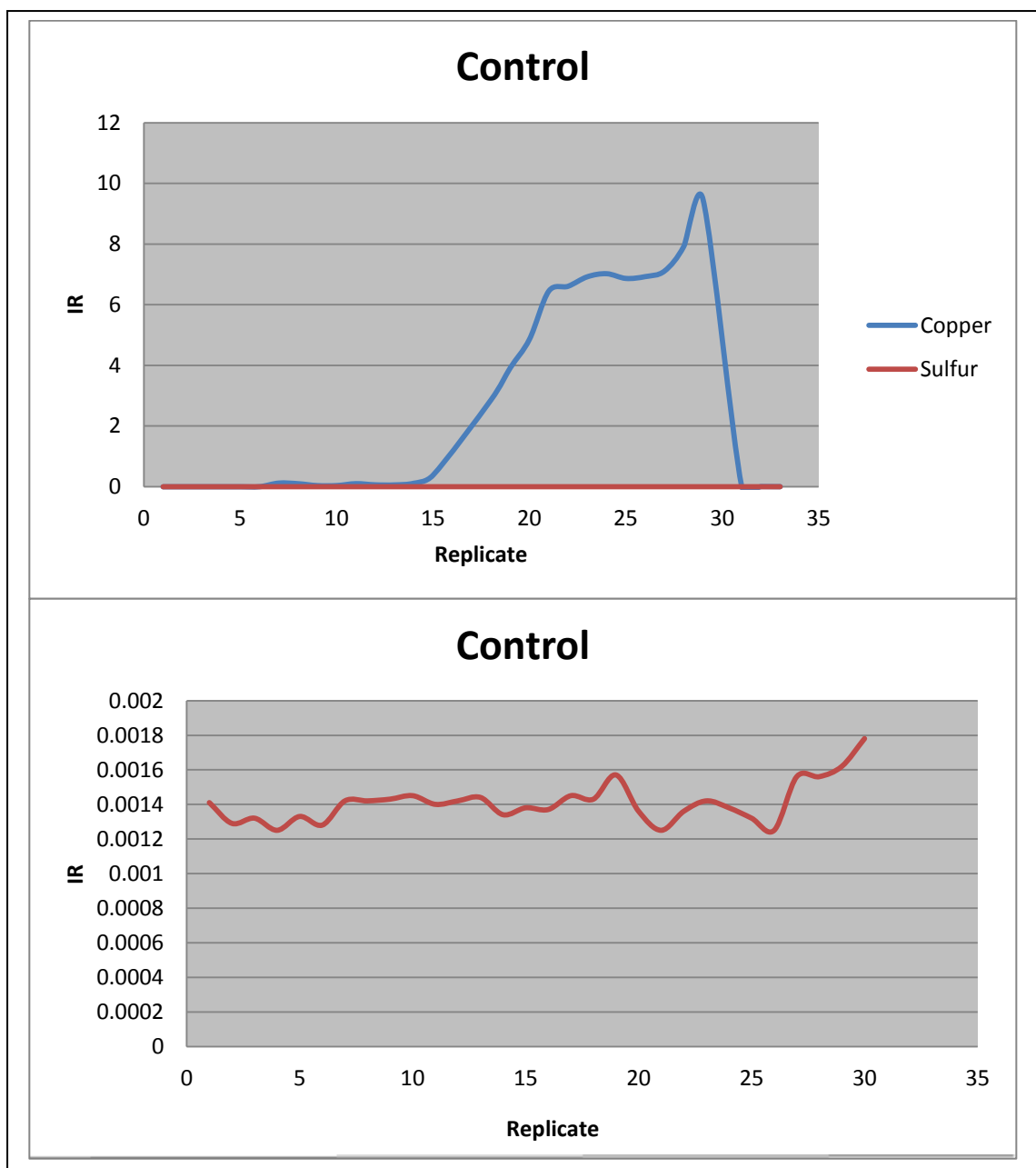
Figure 7. Real time analysis of control drywall sample. Second graph shows magnification of sulfur results.

All fifty drywall samples and their duplicates showed some compound oxidized the copper and turned it black. This compound came from the drywall itself since the tubes were sealed tight and the part of the copper coupon outside of the tube remained unchanged. Also, the copper in the blank and control did not turn black. Based on the research conducted by Tolaymat, El Badawy, and Carson, (2013), the possible

compounds included hydrogen sulfide, bisulfide ions, and/or sulfide ions. All samples had results showing there was sulfur in the drywall that was reduced to volatile sulfide compounds from the moisture present in the tubes. Graphing the real time analysis resulted in the graphs looking one of five ways as can be seen in Figures 8, 9, 10, 11, and 12. The samples that produced graphs that did not look like the expected baseline-peak-baseline shape were re-analyzed and produced the same results. The difference in shapes when graphed could be dependent on which sulfide compound or combinations of sulfide compounds were present in that specific sample of drywall. These compounds included H_2S, CS_2, COS, and SO_2. The shapes of the graphs in Figures 8 and 9 were similar to the results seen in Figure 3 when the sodium sulfide standard was used to develop and modify the method used. This could possibly mean that those samples contained H_2S specifically. To some degree the concentrations of the volatilized sulfide compound could be close to the concentrations of the samples made from the standard. The samples run in duplicate were similar to Figures 8, 9, and 11 as can be seen in Figures 13, 14, and 15. The variations in instrument response when the samples were run in duplicate could have come from the fact that drywall is not necessarily homogenized when made. This means the concentrations of the sulfur in the material could vary depending on where the sample is cut from the piece of drywall. The drywall used to set up the parent sample and the duplicate were from the same wall, but not necessarily cut from the same location.
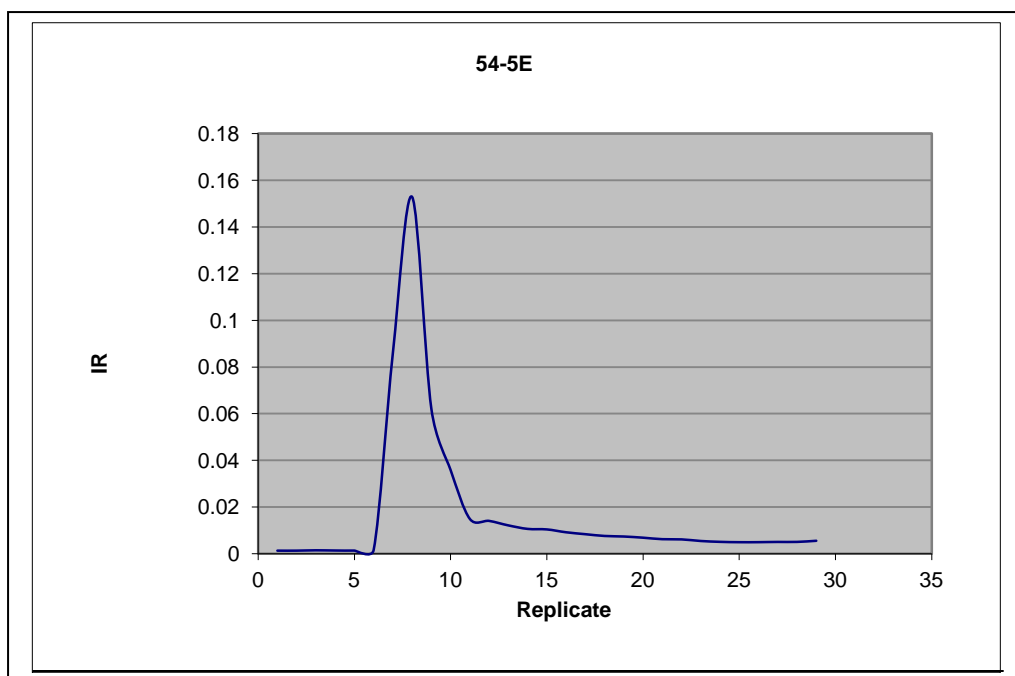
Figure 8. Graph of the instrument response versus the replicate number for sample 54-5E. Twenty-four samples, including this one, had a pattern like this where the initial reading was a baseline, then a peak observed, then it fell back down close to the baseline again.
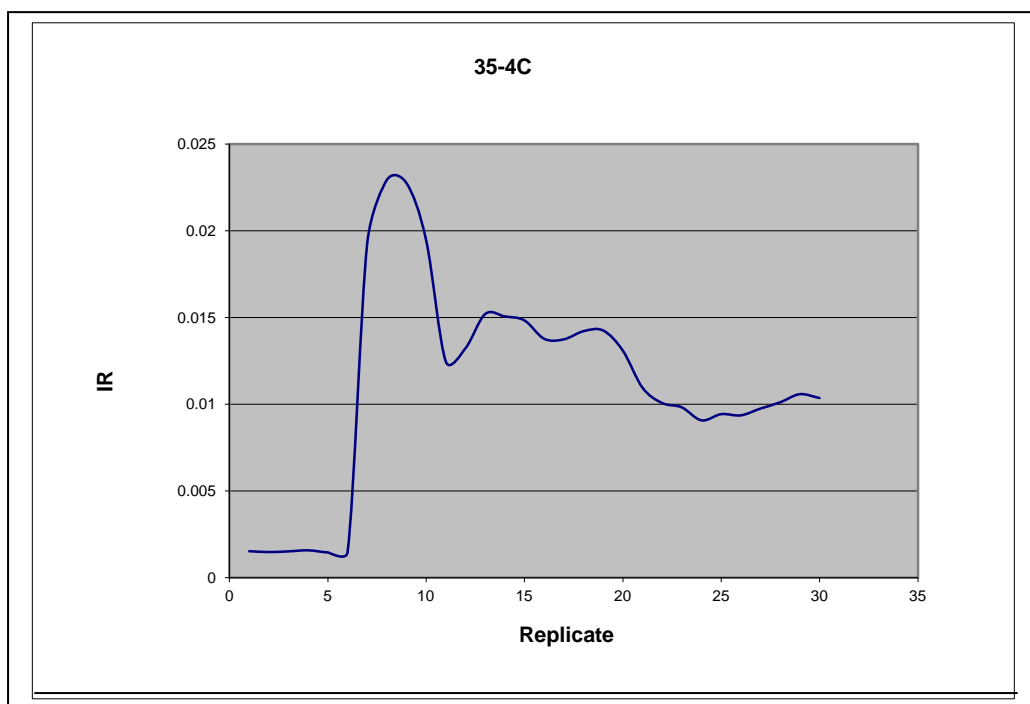

Figure 9. Graph of the instrument response versus the replicate number for sample 35-4C. Ten samples, including this one, had a pattern like this where the initial reading was a baseline, then it peaked, and then it did not quite fall back down to the baseline.
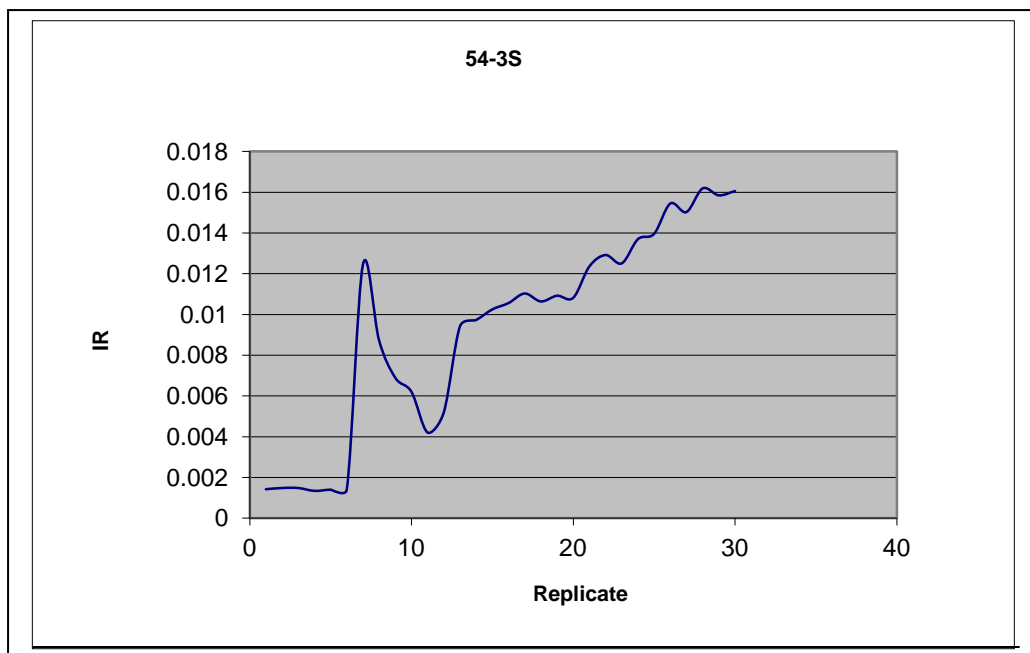
Figure 10. Graph of the instrument response versus the replicate number for sample 54-3S. Nine samples, including this one, had a pattern like this where the initial reading was a baseline, then it peaked, and then it either peaked a second time or looked like it was about to instead of going back down towards the baseline.
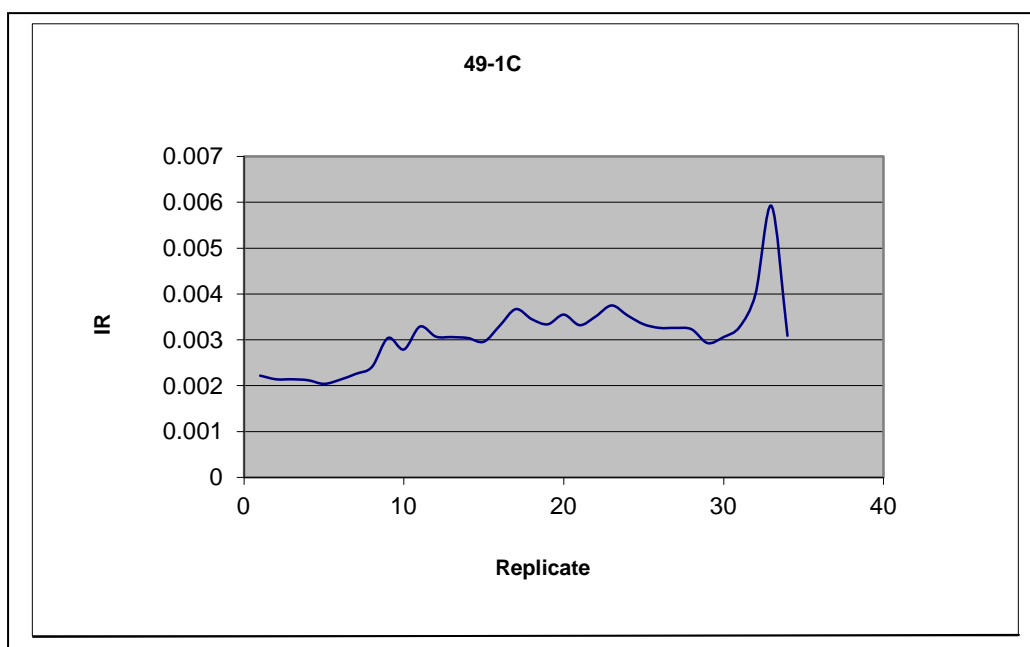

Figure 11. Graph of the instrument response versus the replicate number for sample 49-1C. Five samples, including this one, had a pattern like this where the initial reading was a baseline, then it peaked, and then it fell back down towards the baseline. However, the peak occurred more towards the end of the forty replicates instead of towards the beginning.
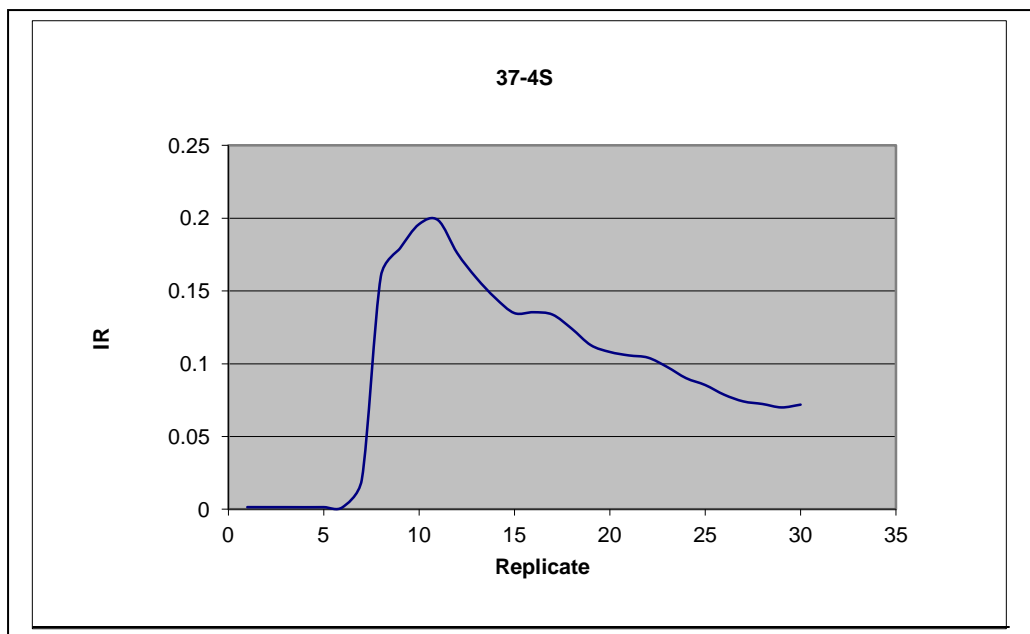
Figure 12. Graph of the instrument response versus the replicate number for sample 37-4S. Two samples, including this one, had a pattern like this where the initial reading was a baseline, then it peaked, and then it fell back down towards the baseline. However, the peak was more broad instead of narrow. These samples may not have completely gone into solution.
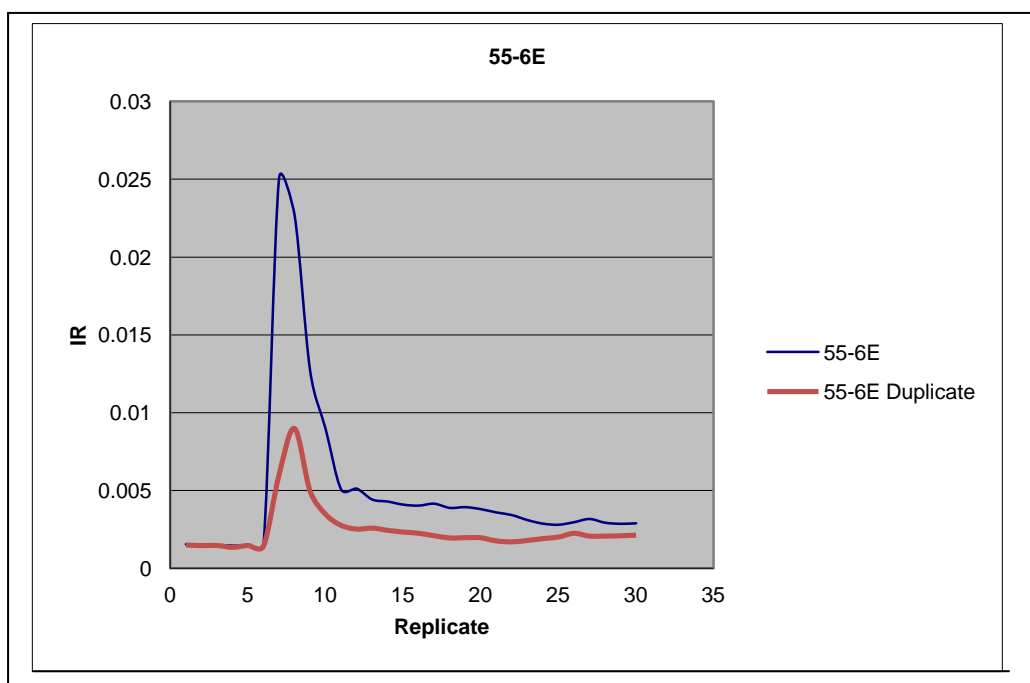

Figure 13. Graph of the instrument response versus the replicate number for sample 55-6E. Three of the samples run in duplicate, including this one, had a pattern like this where the initial reading was a baseline, then a peak occurred, then it fell back down close to the baseline again.
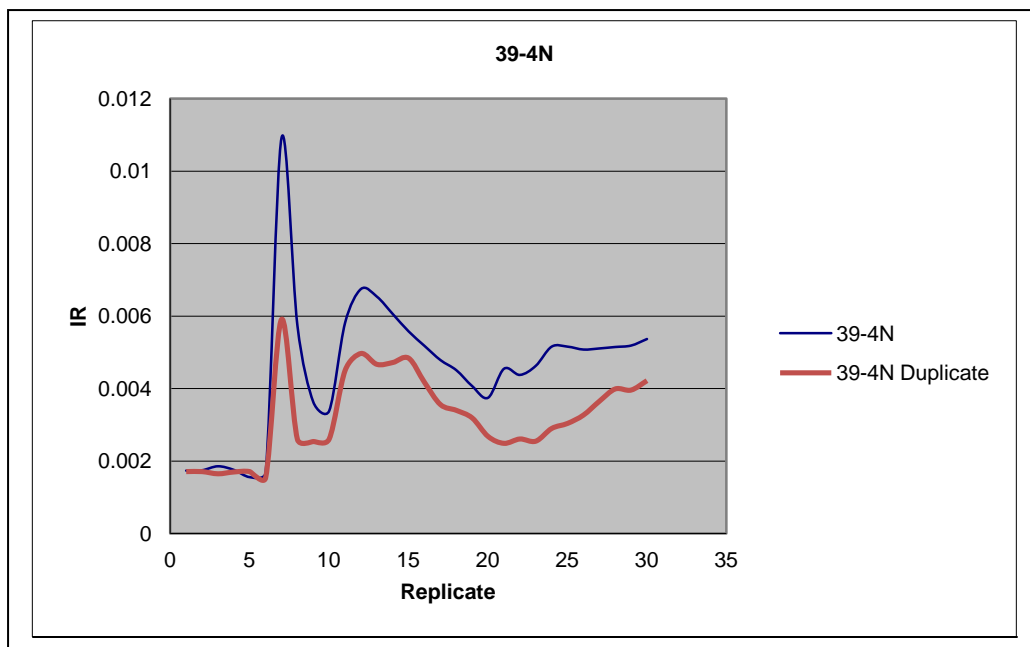
Figure 14. Graph of the instrument response versus the replicate number for sample 39-4N. This sample run in duplicate had a pattern where the initial reading was a baseline, then it peaked, and then it did not quite fall back down to the baseline.
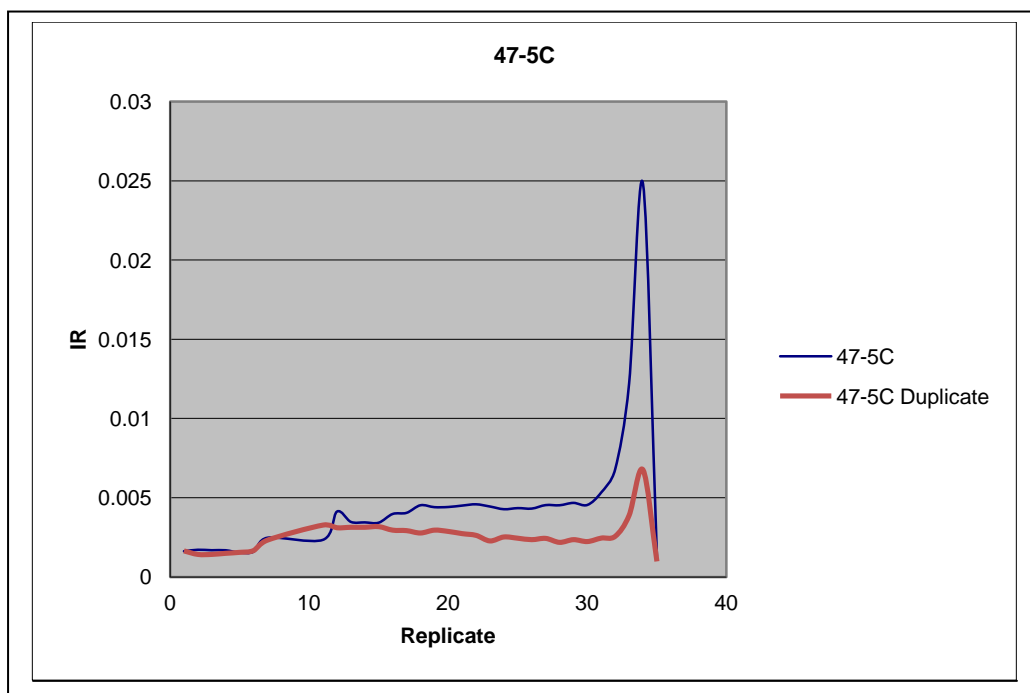

Figure 15. Graph of the instrument response versus the replicate number for sample 47-5C. This sample run in duplicate had a pattern where the initial reading was a baseline, then it peaked, and then it fell back down towards the baseline. However, the peak occurred more towards the end of the forty replicates instead of towards the beginning.

CHAPTER V

SUMMARY

Chinese drywall is still an issue showing up in homes to this day. Although it is no longer imported to the United States, its effects are still very much present. As congressmen and women try to get legislation approved to help those affected by the corrosive drywall, not many have had much success. Not only are people having to spend thousands of dollars to have their homes re-built and appliances replaced, there are also lasting health effects. Not to mention the inconvenience of having to find a temporary home for months at a time depending on how damaged their homes are. Based on previous research, the corrosive compounds found in Chinese drywall include high amounts of strontium, sulfur, and carbonate compounds. The damage to many appliances and even the cause of some health issues result from the volatile sulfide compounds. Since sulfide compounds present in Chinese drywall are causing millions in damages to homes and even health hazards, it is important to develop a way to test drywall to determine if it has the potential to become corrosive or not. Most importantly, the laboratory preparation and analysis of the drywall should be cost effective.

Current researchers have tried using XRF guns, AA, and even an FTIR in order to analyze the components of Chinese drywall. However, these instruments all have disadvantages. The XRF gun seemed to have problems if there were other compounds such as paint and paper on top of the drywall (Allen et al., 2012). Although AA was used to establish a correlation from the XRF results, it has a disadvantage of only analyzing one element at a time. It cannot analyze multiple elements at once like the ICP-AES can, and it cannot check for elemental interferences as readily. It also cannot analyze non

metals, such as sulfur. Although these research methods produce valuable results, they have their disadvantages.

This experiment focused on creating a useable method for analyzing drywall via an ICP-AES. Since current certified digestion methods would produce a false negative for sulfur, a different method was developed. This method used real time analysis to qualitatively analyze the drywall for sulfur. The preparation of the sample also uses fewer reagents and is more cost effective. Between the materials used to set up the samples in a natural environment and the materials used to prepare each sample for real time analysis, it costs less than a dollar per sample. Since it is a non-preparation method it also does not require multiple hours of digestion. However, the amount of time required to analyze the sample is longer when compared to other digestion methods. Each sample in this experiment took about 30 minutes to do 40 replicates. Whereas, samples that are digested can be analyzed in less than three minutes since they can be analyzed in as few as three replicates. A sulfide standard was used to create samples to help develop the method, so the drywall samples would not be wasted. After many trial runs, a method was successfully developed that was able to analyze only copper and sulfur with no worries of interferences from other elements. The number of replicates, along with the exposure time, and wash time were successfully determined with the standard samples too. During the real time analysis, the number of replicates was 40, with the wash time being 50 seconds, and the exposure time being 30 seconds in the low axial view and 1 second in all other views. This modified method was able to qualitatively identify the presence of some sulfide compound in all of the Chinese drywall samples.

Even though each Chinese drywall sample showed evidence of sulfur, the real time analysis results varied once graphed. The shape in the graph looked one of five ways, including a narrow peak, a broad peak, a peak that occurred later on in the number of replicates, a peak whose baseline afterwards went in an upward direction, and a peak whose baseline afterwards did not quite fall back down. Even though this was the case, the majority of the sample results, when graphed, looked like the narrow peak shape. One theory as to why this could have happened is that the way the results looked was dependent on which sulfide compound or combination of sulfide compounds were present in the drywall. These differences could also be accounted for by the fact that some drywall samples may have contained higher levels of sulfur than others since drywall material is not homogenized before it is made. Also, the different sulfide compounds have different solubilities. This means that when the oxidized copper was dropped in the sample solution, the sulfide compounds may have completely volatilized during the 40 replicates for some drywall samples and not for others. The type of acidified water was also tested to see if there was a difference since the acidified water contained both nitric acid and hydrochloric acid and the formation of copper chloride was thought to be a potential issue. However, when one of the samples that were already analyzed was re-run in a solution with just nitric acid, the graph did not change much.

Although this experiment allowed for the qualitative analysis of sulfur in Chinese drywall, there are still areas that could be explored in future research. One could try to determine what specific sulfide compounds were present in each drywall sample by comparing it to other standards, just like the sodium sulfide standard was used to show which drywall samples had hydrogen sulfide, specifically. This was not done in this

project due to the fact that those standards are very hard to obtain. One could also modify

the method or experiment in order to see if the sulfur in the drywall can be accurately

quantified. However, this could be hard to do since it is hard to determine the specific

combinations of sulfide compounds present in Chinese drywall. Quantitation could also

be difficult since the material is not homogenized before making the drywall meaning

concentrations could vary from section to section of the piece of drywall.

This novel method was able to identify the presence of sulfur in Chinese drywall.

It did not produce any false negative results, such as the certified EPA 3050B method

does. It is also a cost effective process for analysis. Each sample costs less than a dollar

to set up and prepare. The standards used in the curve for calibration cost about sixteen

dollars per curve. However, the curve used in this method is stable for about a week and

can be used about four times before it needs to be made again. The identification of the

presence of sulfide compounds in Chinese drywall could help everyone affected by the

use of the corrosive material and even prevent more victims. This method could aid in

preventing millions of dollars more in damage to buildings and appliances. No longer

using this corrosive drywall would also prevent all the health hazards and problems

people have to deal with. Determining whether the drywall used in construction is

Chinese drywall or not could also aid in the investigation of arson and insurance fraud.

There have been cases where people have intentionally set fires to collect insurance on

their destroyed properties and blame it on the use of Chinese drywall. This method could

aid in the process of determining if the claims are valid.

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