LIQUID CHROMATOGRAPHY-TANDEM MASS SPECTROMETRY OF FIRE DEBRIS EVIDENCE AT SUSPECTED CLANDESTINE METHAMPHETAMINE LABORATORIES

By

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Abstract: The "One-Pot" methamphetamine production method involves the combination and use of highly reactive and flammable materials. Individuals attempting this method are creating clandestine laboratories within residences and other occupied structures, and the likelihood of a subsequent fire puts anyone nearby at risk. In the State of Oklahoma, if the production of methamphetamine causes a fire, the crime falls under the first degree arson statute, which can involve a prison sentence of 35 years, as opposed to 7 years for the production of drugs. The ability to detect methamphetamine and the One-Pot precursors in fire debris would strengthen the arson investigation. One-Pot methamphetamine reactions were carried out and the liquid and solid products were used to recreate a fire. Small burn cells were used to represent a residential environment. Several fire debris sample types were collected, including wall wipe samples, burned bottles, wood, and carpet. Each sample was analyzed for ignitable liquids using headspace extraction and gas chromatography-mass spectrometry (GC/MS). Following arson analysis, liquid chromatography-tandem mass spectrometry (LC-MS/MS) was used to detect methamphetamine and pseudoephedrine, the methamphetamine precursor, in the fire debris. Additionally, fire debris samples were provided to local law enforcement and GC/MS was also able to detect methamphetamine in the fire debris. This work demonstrates that fire debris analysis can prove the presence of clandestine methamphetamine laboratories that result in arson fires.

TABLE OF CONTENTS

LIST OF TABLES

Table Page

LIST OF FIGURES

Figure Page

CHAPTER I

INTRODUCTION

Methamphetamine, a powerful stimulant drug, has kindled into a severe problem over the past several decades. According to statistics tabulated by the Drug Enforcement Agency (DEA), over 85 000 methamphetamine laboratory incidents were reported from 2004-2011.[1] Among these incidents, Tulsa County in Oklahoma has the highest reported number at 979. As an easily synthesized drug, methamphetamine, or *meth* for short, can be produced in a variety of ways. According to Heegel and Northrop, "Newer methods of manufacturing appear as restrictions are placed on common manufacturing ingredients."[2] While preventive actions are negated by new or updated methods, corrective actions should be pursued to improve investigations involving methamphetamine production. Recently, a popular technique is the "One-pot" method, which involves the use of products that can be found in local retail stores. The necessary starting material, pseudoephedrine or *pseudo*, a medicine used for treatment of nasal congestion, is sold at pharmacies. As a result of the easy access to the ingredients, the One-pot method is preferred within clandestine laboratories. Besides the dangers of using the methamphetamine itself, production and manufacture present the potential for serious risks. Perhaps the most hazardous threat is the possibility of a resulting fire.

The One-pot method, as the name suggests, produces methamphetamine by adding all of the reagents to a single pot or bottle and allowing the reaction to proceed. Despite the simplicity of the procedure, necessary materials such as diethyl ether or camping fuel, both of which are highly flammable solvents, increase the likelihood of starting a fire.

Commonly, methamphetamine manufacturers or "cooks" use an empty Gatorade bottle as the reaction vessel. A combination of the plastic lining and the pressure of the reaction can cause the bottle to fail, and the ingredients spill into the immediate area. The highly reactive lithium strips, a necessary ingredient, ignites upon contact with the atmosphere and causes the organic solvent to catch flame. With the majority of methamphetamine laboratories operating within households or apartments, any ensuing fire would consume the residence.[3] At a post-fire crime scene, debris suspected to contain trace amounts of volatile solvents is collected for analysis of ignitable liquids.[3] According to Title 21-1404 of the Oklahoma Statute, "Any person who, while manufacturing, attempting to manufacture or endeavoring to manufacture a controlled dangerous substance...destroys in whole or in part, or causes to be burned or destroyed, or aids, counsels or procures the burning or destruction of any building or contents thereof, inhabited or occupied by one or more persons whether the property of that person or another…" shall be imprisoned up to 35 years.[4] This first-degree arson penalty is much more severe than the punishment for drug manufacturing, which is only 7 years in prison according to the Oklahoma Controlled Substances Act.[5] Proving that the production of methamphetamine was the cause of the fire could keep the suspect away from the community for a longer period of time.

Collecting evidence for the detection of methamphetamine and pseudoephedrine would have multiple benefits. Laboratory analysis of fire debris for methamphetamine and pseudoephedrine could provide arson investigators with the starting location of the fire, if not already known. In addition, proving that the presence of methamphetamine production caused or enhanced the fire would lead to steeper penalties for the suspect(s) in the case. However, the possibility of testing arson evidence for methamphetamine and pseudoephedrine has yet to be completely developed and implemented.

The purpose of this arson study was to test the theory of methamphetamine and pseudoephedrine detection in burned evidence samples collected from controlled fire experiments. The research team performed methamphetamine production, fire ignition, and suppression in repeated manners to remove unnecessary variables. Methamphetamine was manufactured in a safe environment at the Forensic Toxicology and Trace Laboratory (FTTL) located within the Oklahoma State University-Center for Health Sciences (OSU-CHS). Two solvents, diethyl ether and Coleman fuel, a type of camping petroleum, were used for methamphetamine production. Commonly used Gatorade bottles were emptied and filled with One-pot products. Each bottle was placed in identical structures or "huts" which were used to represent non-variable residential environments. Several types of samples, such as wood, carpet, drywall etc., were collected to include typical arson evidence from house or apartment fires. The mock fires had various burning durations to represent the unpredictable timing of fire-fighter response.

After sample collection, methamphetamine and pseudoephedrine drugs were extracted and analyzed at the FTTL with Liquid Chromatograph-Tandem Mass Spectrometer (LC-MS-MS) instrumentation. Cumulatively, the research answered the following questions: 1) Can evidence collected at a suspected methamphetamine lab fire detect methamphetamine and or pseudoephedrine drugs? 2) Would more severely charred or burned samples show a decrease in analytical detection? 3) Are certain sample types more likely to contain the drugs of interest? 4) Can a detection method be applied to current forensic laboratories? The answers provided by this study will provide arson investigators and crime laboratories with valuable information regarding collection and testing of fire debris samples for the detection of methamphetamine and pseudoephedrine.

CHAPTER II

REVIEW OF LITERATURE

Introduction

Investigation and evidence testing for methamphetamine, particularly drug detection in arson cases, is not fully understood. Popular techniques to produce methamphetamine include the P2P method, Red P method, Nazi-Birch reduction, and the more common One-pot method. Required materials and knowledge vary drastically among these techniques. All of the products and materials for the One-Pot method are easily accessible, which makes it possible for anyone to start producing meth. However, several of the ingredients involved are highly flammable. Many individuals attempting the One-Pot method lack a safe environment, and decide to perform the reaction within a household or apartment. An ensuing fire would create a dangerous situation for inhabitants and ultimately destroy the residence.[6] Depending on the amount of damage, the cause of the fire may be difficult to determine. Arson investigators collect samples suspected to contain trace amounts of volatile or flammable solvents to identify the starting location of the fire.[3] The possibility of testing evidence for the presence of methamphetamine and pseudoephedrine, where its production was likely to cause the fire, has yet to be completely developed and implemented.

History and Progression

The emergence of methamphetamine has been thoroughly monitored in the United States. One common concern is that methamphetamine labs are extremely flammable. With a methamphetamine study from the University of California, Los Angeles, Gonzales et al provided statistics and trends. The study estimated meth-related costs at $23.4 billion in 2005, ranging from criminal justice expenses to clean up costs. Fire damages account for part of the estimated cost, with methamphetamine labs often discovered because of consequent fires. In fact, as much as 15% of methamphetamine labs were identified in one county because of related fires.[7] These statistics demonstrate both the prevalence of methamphetamine and the likelihood of consequent fires. The study also involves a historical timeline of meth, explaining the changes over time. Important observations include the almost relentless altering of methamphetamine experiments, productions, and sales to deter law enforcement efforts.[7] Once pseudoephedrine became a starting material, legislation followed in most states, which limited the amount sold to individuals. In response, methamphetamine manufacturers hired individuals to purchase pseudoephedrine to obtain larger quantities. Gonzales et al conclude that methamphetamine's associated dangers will continue to be an issue for the United States.[7] Since prevention efforts have ultimately failed, investigative and prosecution efforts should be improved.

More recent studies about the methamphetamine problem indicate similar historical timelines. Reviewing the cyclical rise and fall of methamphetamine production and seizures, Maxwell and Brecht concluded that every decline is associated with a federal restriction of materials used to produce meth.[8] Although restrictions brought methamphetamine production to a halt, methamphetamine users and addicts were still present. Unfortunately, most declines were immediately followed by an incline because methamphetamine manufacturers discovered a way to avoid the restriction or developed a new technique.[8] The study indicates that the incline is likely to occur in geographical areas that have had a prior methamphetamine problem.[8] The high demand and recent incline proves that methamphetamine is still a problem in today's society.

Shukla et al agree that methamphetamine manufacturers adapt in response to federal or state legislation and suggest that the regulatory efforts are "short-term and temporary."[1] Therefore, governmental pursuit of additional regulations would likely become ineffective. The study also highlights the impact of the Internet. Individuals can purchase starting materials online and share their recipes and comments.[1] Computers and smart phones with Internet access provide easy access to instructions for a methamphetamine cook. Additionally, when new legislative restrictions are introduced, the Internet can essentially become a discussion tool for anyone in the US. Once a new and successful method is developed, news spreads quickly among the online methamphetamine community. Internet accessibility may explain the failure of government regulations to reduce methamphetamine prevalence. Shukla et al conclude that there is no easy solution to the methamphetamine problem and that more studies are necessary.[1]

Health Concerns

Besides the potential fires or explosions, methamphetamine production also has related health risks. Not only do the cooks put themselves at risk, but they also put family members or friends in the same residence at risk as well. Related studies and reviews have been conducted about health concerns, especially in regard to innocent children. In 2003, Karen Swetlow wrote that children suffer from inhaling toxic fumes, living among the chemical spills, and even breathing second-hand methamphetamine smoke.[9] Aside from the hazards of the procedure, other factors can also have negative impacts. Trends show that children in methamphetamine environments are more likely to experience abuse or neglect. Additionally, the children experience violent behavior, as many manufacturers own firearms for protection of the illicit product.[9] In a case involving a methamphetamine fire, a positive determination of methamphetamine within the household might save any children or innocent members from future health risks. Swetlow mentions that some states have passed child endangerment legislation regarding methamphetamine labs.[9] Although this study pertains to the required actions of child protection services, it explains the severity of health effects and the necessity to solve the methamphetamine problem.

Thrasher and Burgess conducted a more recent poison study in 2009 to compile more information about the symptoms of methamphetamine exposure. Results not only compared adults versus children, but examined law enforcement personnel as well.[6] Common symptoms included headaches, nausea, and vomiting. More importantly, both methamphetamine cooks and law enforcement agents showed high healthcare utilization rates.[6] Methamphetamine lab fires can cause similar health problems because toxic reagents can develop into the atmosphere upon burning. A concluding statement of the study indicates the importance of proper cleanup of the scenes.[6] However, at some fire scenes, the destruction may leave little evidence of a methamphetamine lab. Even for fire scenes with the slightest suspicion, collecting evidence would be crucial to test for the presence of methamphetamine because it could create more prosecuting opportunities.

Production Techniques

Over methamphetamine's history, the production technique has changed drastically. Some changes were due to government regulations, such as moving away from the Phenyl-2-Propanone (P2P) method when methamphetamine became a Schedule II controlled substance in 1980.[1] When P2P, a crucial starting material, became less available, a new method using pseudoephedrine became the norm. The "Nazi" and "Birch Reduction" are two popular examples of names assigned to the lithium-ammonia reduction process.[10] The Birch Reduction Method uses anhydrous ammonia to produce methamphetamine, as proven in a study conducted in 2004.[11]

Using this method, Bradley Crow from the Kansas Bureau of Investigation completed a single experiment to determine methamphetamine yield. The instrument utilized in the post-reaction analysis was a gas chromatograph equipped with a mass spectrometer (GC/MS). Results showed considerable yield at 39%, but more importantly, determined that unreacted pseudoephedrine was present.[11] A similar instrument was used in a study conducted by the Washington State Patrol Marysville Crime Laboratory. Person and Knops focused on ammonia generation and came to the important conclusion that water generated throughout the reaction would not prohibit pseudoephedrine from converting into methamphetamine. However, using liquid ammonia in an aqueous solution, thus an abundance of water, would not be sufficient for the conversion.[12] A detailed understanding of the starting products is necessary to produce methamphetamine effectively.

New and simpler methods using ammonia generation started to become popular. Later in 2004, Person and Knops produced another study with Northrop and Sheridan, and this time involving the "One-pot" methamphetamine method, which was growing in popularity. The authors responded to a request from the Snohomish Region Drug Task Force, regarding the ability of ammonia to be generated within the reaction.[13] Results from the study proved successful as methamphetamine was presumptively detected after a reaction of two hours. A GC/MS instrument was used to identify methamphetamine and pseudoephedrine. Additionally, an experiment was allowed to react overnight and displayed a larger methamphetamine peak on the chromatogram than the two hour experiment.[13] Overall, the study provided a successful "One-pot" method procedure that can be replicated for future studies. A second study on the same method was conducted a year later by Heegel and Northrop. The question at hand was whether the multi-ingredient pseudoephedrine tablets, which contain other drugs to combat multiple health issues, should be altered to isolate the drug of interest.[7] To answer, the authors conducted four varying pseudoephedrine product experiments without altering the drug. The results showed that methamphetamine could be produced without extracting the pseudoephedrine beforehand.[7] Also, the conclusions demonstrated the simplicity of the "One-pot" method. A quick and cheap method to produce a high demand drug is appealing to clandestine chemists as well as individuals looking for economic gain.

Investigation

As the techniques for methamphetamine production continue to change and adapt, investigators must strive to learn the relevant evidence samples. In an FBI Law Enforcement Bulletin, Dennis Hanwell writes about investigating and searching scenes of suspected methamphetamine production. From a safety standpoint, "[t]he proper cooperation, planning, and input from various agencies prove critical to the success of the investigation and the safety of all concerned."[14] Hanwell stresses informing all individuals involved and following a set procedure. Knowledge of which aspects of the methamphetamine experiment are hazardous does not provide a complete understanding. Investigators must be able to collect the appropriate samples for drug analysis.

One study from the University of British Columbia reviewed the available technologies to examine airborne molecules of methamphetamine. After a complete review of the various production techniques, the authors decided that ammonia and organic solvents are among the target gases.[15] Highly detailed sensors have the ability to detect compounds within the atmosphere. Man et al used many different sensors such as ion mobility spectrometry, photoionization detection, and Fourier transform infrared spectrometer (FTIR).[15] Unfortunately, such detection instruments are usually quite costly. On the other hand, the review concludes that sensing technology is a successful method to detect the presence of a methamphetamine lab. The authors also suggest the possibility of locating clandestine environments after sensing spiked levels of a target gas.[15]

A detailed study conducted in Colorado helped determine what type of samples can be collected for methamphetamine analysis. VanDyke et al developed a study within an actual household to examine the scene within a 24-hour period.[16] Although a study of this nature may lack validity, the uncontrolled environment of a household generates reliability. To replicate an actual clandestine scene, the research team performed methamphetamine experiments in one room or region of the household. On day 1, two methamphetamine batches were produced using a lithium-ammonia reduction called the "Red Phosphorus" method.[16] Although the technique is not the same as the more recent and popular "One-pot" method, the study still provides insight about processing the crime scene. On day 2, the researchers started collecting evidence, which included atmosphere, wipe, and vacuum samples.[16] Atmosphere samples were collected with a pump, wipe samples with some sort of gauze or cloth, and vacuum samples drawn from the carpeted areas.[16] Based on the results, atmosphere or air samples can be collected and methamphetamine can be detected for at least 24 hours after production. The potential to inhale toxic fumes and methamphetamine is a serious health concern for investigators. Airborne methamphetamine particles were determined to be rather small and thus have the ability to be inhaled and absorbed by anyone near the production site.[16] The next collection type was wipe samples, which were collected from various sources, including the researchers themselves. Wipe results showed positive methamphetamine detection in many areas of the house and on the researchers.[16] One of the main accomplishments of this study was determining that investigators can collect multiple sample types to prove the existence of a methamphetamine lab. However, one study limitation is that the investigators used a perfectly stable location. Attempting to collect viable samples such as airborne particles and surface wipes at an actual methamphetamine fire scene may be difficult. Another limitation mentioned in this study's discussion is that every methamphetamine lab is different, and any research project must be evaluated on an individual basis.[16]

Conclusion

The history of methamphetamine is a battle of ups and downs with federal and state legislation. Based on review of the literature, methamphetamine is still a significant problem and is unlikely to go away soon. Though health concerns are not fully understood, the effects are recognized; and the severity increases the need to protect any affected communities. Clandestine chemists have developed cheap ways to produce methamphetamine and the methods are shared quickly via the Internet. The simplicity surrounding methamphetamine production has allowed individuals to make the drug in the comfort of a household or apartment. Anyone, especially an uneducated cook, has the potential danger of starting a methamphetamine fire. Research studies have determined multiple evidence types that can be processed and collected at methamphetamine lab locations. However, the question of whether fire debris can be analyzed for methamphetamine and pseudoephedrine has not been answered.

CHAPTER III

METHODOLOGY

Introduction

This study contained four research stages: preparations, field tests, laboratory analysis, and forensic application. The first stage involved the production of methamphetamine. Due to the illicit nature of the topic, law enforcement personnel are the only individuals provided with details of the procedure. The second research stage involved fire recreations and arson debris collection. The third stage involved laboratory analysis using Liquid Chromatography-Tandem Mass Spectrometry (LC-MS-MS) of the experimental samples from the fire recreations. Lastly, the fourth stage consisted of the samples being sent to local crime laboratories for drug analysis. The research did not involve human subjects; therefore standards and guidelines from the Institutional Review Board (IRB) will not be mentioned. Combining all four stages created an experiment with a known presence of methamphetamine and an opportunity to determine if post-fire detection was possible in several laboratory settings.

Preparation steps utilized materials and equipment from the Forensic Toxicology and Trace Laboratory (FTTL) at Oklahoma State University-Center for Health Sciences (OSU-CHS). Methamphetamine products obtained from the FTTL were stored and transported to the Fire Research Laboratory (FRL), a facility operated by the Bureau of Alcohol, Tobacco, Firearms, and Explosives (ATF). Field tests provided fire debris evidence. Upon experimental completion at the FRL, samples were collected and transported to the FTTL.

Following a simple extraction and preparation, the samples were analyzed for methamphetamine and pseudoephedrine with LC-MS-MS instrumentation, a standard analytical technique in toxicology.

After arson and drug analyses, fire debris samples were sent to the Tulsa Police Department Crime Laboratory and Oklahoma State Bureau of Investigation Crime Laboratory. Current instrument technology in each respective lab was used to attempt methamphetamine and or pseudoephedrine detection.

Preparations- methamphetamine production

Before arson analysis could be performed, methamphetamine was produced in a laboratory environment. Due to the popularity of the method, methamphetamine was produced using One-pot methodology and required the following materials: pseudoephedrine, an organic solvent (diethyl ether or Coleman fuel), ammonium hydroxide, sodium hydroxide, lithium, and water. Equipment included: chemical fume hood, pressurized reaction vessel with tube-fitting cap, pressure release valve, stir plate, magnetic stir bar, ring stand, plastic funnel, and forceps. Each equipment piece was used to ensure safety and limit interaction with the overall procedure. System pressure was released after two hours of reacting. Lithium strips were removed via forceps from the reaction. The solvent was filtered through a plastic funnel to separate solid waste from liquid product. Two differing solvents were packaged separately as well as their respective solid waste. Again, to avoid abuse, the exact steps required for methamphetamine production will not be discussed.

Field Tests- fire recreations in controlled environment

ATF agents transported methamphetamine products to the (FRL) in Maryland. In addition to the previously prepared materials, the following items were needed: wood, drywall, carpet, padding, empty Gatorade bottles, blowtorch, cameras, and evidence collection supplies. FRL research staff built small "huts" to mimic actual residential compartments. An important aspect of each hut was that it contained a wooden structure, drywall, and carpet with pad. These materials are commonly found in homes and apartments. Additionally, small wooden tables were built and placed in each of the four huts to demonstrate residential furniture. See Figure 1 for a photo of the residential hut.

Figure 1. Residential hut. Each hut was made of wood and contained drywall, carpet, etc. which are commonly found in residences. Small wooden tables, as seen in the bottom left, were also used to represent furniture.

The previously prepared methamphetamine products from the first research stage were added to 20 oz. Gatorade bottles. Approximately, 350 milliliters of diethyl ether and 20 grams of solid waste were added to each of the first four bottles, labeled E1-E4. Another group of four Gatorade bottles each contained the same amount of product, but from Coleman fuel solvent reactions, and were consequently labeled C1-C4. A single bottle was used for each experiment, giving a total of eight methamphetamine fires.

One at a time, Gatorade bottles were placed on a documented and designated location of the wooden tables located in the residential huts. The first two experiments of each solvent were ignited via blowtorch and allowed to burn for several minutes. To initiate each fire, a suppression team member used a blowtorch to burn a hole in the side of the Gatorade bottle below the liquid line. The solvent would shoot out of the hole due to reaction pressure, and ignite against the drywall interior. Flames would then stretch to the rest of the hut. See Figure 2 on the following page for an example of residential hut on fire. If the bottle itself did not catch fire within 30 seconds, a suppression team member tipped the bottle to one side to represent complete bottle failure. After a minute or two of burning, the fire suppression team extinguished the fire using water. The second two experiments of each solvent were identical to the first experiments except additional cardboard and paper materials were placed underneath the wooden table to ensure more thorough burning.

Figure 2. Residential hut on fire. After each One-pot Gatorade bottle was ignited, the fire would start out slow, but then evolve into large flames that you see in this photo.

After each hut was deemed safe and absent of any fire or smoke, the interiors were photographed and documented as if actual arson crime scenes. ATF agents then proceeded to collect and package several types of evidence. Samples included solid product from the Gatorade bottle, wood from the table, carpet and pad section that likely contained spilt solvent, and wall wipes. See Figures 3, 4, and 5 for photographs of solid product, wood, and carpet samples respectively. For the solid product, forceps or tweezers were used to scoop waste or "sludge" from the Gatorade bottle. For wood samples from each table, a burnt section was cut with a saw. For carpet and pad, a box cutter was used to cut a section. For a wall wipe, a piece of gauze was dipped in sterile water and wiped up and down the walls of each residential hut. Every sample, [see Table 1 for a complete list], was appropriately labeled and packaged in a clean, empty paint can.

Figure 3. Burned solid methamphetamine waste sample collection. The photo depicts the remnants of the One-pot Gatorade bottle post-fire. The white substance is solid methamphetamine waste or "sludge."

Figure 4. Burned wooden table sample collection. The photo depicts the area of the small wooden table that was sawed off and collected for analysis.

Figure 5. Burned carpet sample collection. The photo depicts the area of the carpet that was cut and collected for analysis.

Table 1. **Sample collection**. C1-C4 represents the four experiments that involved Coleman fuel. E1-E4 represents the four experiments that involved diethyl ether. A check mark designates that the sample was collected.

Sample	**C1**	**C2**	**C3**	**C4**	**E1**	**E2**	**E3**	**E4**
Sludge	X	X	X	X	X	X	X	X
Wood	X	X	X	X	X	X	X	X
Carpet/Pad	X	X	X	X	X	X	X	X
Wall Wipe	X	X			X	X		

In addition, burned and unburned blanks of each sample type, with the exception of wall wipes, were prepared and stored separately. All evidence was transported to the FTTL in Tulsa, Oklahoma.

Arson Analysis- sample extraction at FRL

For the diethyl ether tests, each sample can was heated at 65°C for 10 minutes in a Yamato brand, model DKN600 constant temperature oven. A one microliter sample was drawn from the can using an airtight syringe. The sample was injected into an Agilent Technologies, Incorporated 6890 Gas Chromatograph coupled with a 5972 Mass Spectrometer (GC-MS). The gas chromatograph was equipped with a J&W DB-1MS (methyl siloxane) capillary column. This column was 30 meters long; had an internal diameter of 0.25 millimeters; and a film thickness of 0.25 micrometers. The split ratio for each injection was twenty-to-one. The carrier gas was ultrahigh purity helium. The injection port was set at 250°C. During each run, the oven was held at 35°C for four minutes; ramped at 10°C/minute to 100°C; and held at 100°C for thirty seconds. The transfer line temperature between the gas chromatograph and the mass spectrometer was held at 280°C. The mass spectrometer scanned from 15 to 150 atomic mass units.

For both the diethyl ether tests and the Coleman fuel tests, each sample was extracted using passive headspace concentration with an activated charcoal strip. The activated charcoal strips were purchased from Albrayco Laboratories, Incorporated of Cromwell, Connecticut. The strips were cut in half using a surgical blade. Both halves of charcoal strip were suspended on a paper clip. Then, one paper clip assembly was placed in each can containing a sample collected from the structure. In order to do this, a magnet was placed on the outside of the can lid. The paper clip assembly was then magnetically attached to the inside of the can lid. The lid was placed on the can, and the can was sealed using a rubber mallet.

Each sample was heated at 65°C for 16 hours in the Yamato constant temperature oven. After 16 hours, the cans were removed from the oven and allowed to cool to room temperature. The charcoal strip was removed from the quart can, placed in a vial and extracted with approximately 400 microliters of carbon disulfide. The samples were then analyzed using the GC-MS described above. One microliter samples were injected into the GC-MS. The split ratio for each injection was twenty-to-one. The injection port was set at 250°C. During each run, the oven was held at 40°C for two minutes; ramped at 5°C/minute to 120°C; then ramped at 12°C/minute to 300°C; and held at 300°C for five minutes. The transfer line temperature between the gas chromatograph and the mass spectrometer was held at 280°C. The mass spectrometer scanned from 15 to 100 atomic mass units prior to the solvent delay and 33 to 300 atomic mass units after the solvent delay. The total ion chromatogram (TIC) and extracted ion profiles (EIP) were used to evaluate the data.

Drug Analysis- sample extraction at OSU

For complete analysis, the following equipment was needed: analytical scale, centrifuge tube, methanol, graduated cylinder, vortex/mixing instrument, centrifuge, and pipette. All evidence types were extracted in the same manner. Appropriately sized samples were separately placed into test tubes with caps. Blanks were also analyzed to make certain that any detection of drugs was due to their presence in the arson samples and not from laboratory contamination. For sludge, 0.5 grams from each fire experiment was added to each sample tube. Sludge samples for C1, C3, and E3 were the only experiments with less than 0.5 grams. The samples contained 0.20, 0.45, and 0.30 grams respectively. 5 milliliters of LC-MS-MS running buffer (50% acetonitrile, 50% water, <1% formic acid and ammonium formate) were added to each of the sludge samples. Wood and carpet/pad samples were cut into small enough pieces to fit into the test tubes. Carpet and pad samples were combined into a single sample type (carpet) because the two could not be distinguished after the fire. 10 milliliters of running buffer were added to each wood and carpet sample. A larger amount of running buffer was needed due to the sample type absorbing the running buffer. The entire wall wipe (gauze) that was used did not require cutting or sectioning. 25 milliliters of running buffer were added to each wall wipe sample. A larger amount was needed because the gauze absorbed some of the liquid.

For extraction, each tube was vortexed and then rocked for 10 minutes to ensure that the running buffer made sufficient contact with the entire sample. The tubes were centrifuged for 2 minutes at 2400 revolutions per minute (RPM). The supernatant was collected and each was diluted in additional running buffer for analysis. A dilution was necessary to ensure that the instrument would not become contaminated with a high drug concentration. An internal standard solution was prepared using Methamphetamine D-5 and Pseudoephedrine D-3, which are deuterated forms of each drug. 50 microliters of internal standard was added to 50 microliters of each sample and vortexed to ensure thorough mixing. 20 microliters of each sample were injected into the LC-MS-MS instrument.

A set of known calibrators were run with every sample set. Each calibrator varied in concentration of equal parts of methamphetamine and pseudoephedrine. The varying concentrations were: 500, 100, 50, 10, 5, and 1 nanogram per milliliter (ng/mL). Similar to the sample preparation for the fire debris samples, 50 microliters of internal standard were added to 50 microliters of each calibrator. Each negative control or blank samples included wood, carpet, wipe, and running buffer. Wood and carpet each had an additional negative control that was burned at the FRL. Internal standard was added to every negative control sample. 20 microliters of each calibrator and negative control were injected into the LC-MS-MS instrument separately.

An LC-MS-MS instrument was used to detect the drugs of interest. Acetonitrile was used for the organic solvent and instrument-grade water was used for the aqueous solvent. Each solvent contained small amounts, less than or equal to 1% by volume, of ammonium formate and formic acid. Overall, the instrument method was two minutes in duration with the majority of flow at 50:50 of each solvent. However, the flow was increased to 95% organic solvent for a minute to ensure all drug molecules were pushed through the column.

Data Analysis- compiling results and statistics at OSU

After completion of the LC-MS-MS instrument method, peak shapes and areas were examined using Analyst Software. Prism, a statistical computer program, was used to determine best linear weighting for each of the analytes. Data was compiled into a Microsoft Office Excel spreadsheet for calculation purposes. Quantitation and Multiple Reaction Monitoring (MRM) ratios were formulated and examined for accuracy and precision, within a 25% error window. All data obtained was recorded.

Drug Analyses- sample extraction at TPD and OSBI

At the Tulsa Police Crime Laboratory, carbon disulfide samples (E1) from the arson analysis were diluted with additional drug-free carbon disulfide and analyzed using Gas Chromatography-Mass Spectrometry. Actual carbon strips from the fire debris in E1 were extracted using methanol and analyzed using the same instrumentation.

At the Oklahoma State Bureau of Investigation Crime Laboratory, carbon strip samples (E2), which had contained carbon disulfide from the arson analysis, were extracted with additional carbon disulfide. Each sample was analyzed via GC-MS instrumentation. Fire debris samples in E2 were soaked in methanol, and the resultant methanol was analyzed using the same instrumentation.

Conclusion

Laboratory produced methamphetamine was introduced to a mock residential fire, and fire debris samples were extracted to be analyzed for ignitable liquids and drugs of interest. By using the One-pot method to produce methamphetamine and other reaction products, the fire recreations provided a better representation of actual methamphetamine fires. Various sample types were collected to determine if any would yield trace amounts methamphetamine and or pseudoephedrine following laboratory analyses.

CHAPTER IV

FINDINGS

Arson Analysis- fire debris results

Upon GC-MS analysis, every sample collected, with the exception of E3 Carpet & padding and C1 trim, demonstrated positive results for an ignitable liquid. See Table 2 for a list of samples tested and corresponding headspace results. Each positive result demonstrated a peak for Coleman fuel or Starting Fluid (diethyl ether). The GC/MS accelerant data was reviewed for peaks that indicated the presence of methamphetamine or pseudoephedrine. The bottle sample from C1 contained a peak consistent with ephedrine/pseudoephedrine, and the bottle samples from E1 and E2 had peaks that were possibly consistent with methamphetamine. The accelerant analysis was qualitative and not qualitative and contemporaneous drug standards were not run.

Table 2. Arson Analysis Results. Several samples from each fire experiment (Test) were analyzed. The sample area describes the sample type. For the Coleman experiments (C1-C4), each sample was extracted using a charcoal strip and passive headspace methodology. For the diethyl ether experiments (E1-E4), each sample was extracted using both heated and passive headspace methodologies.

Test	Sample Area	Heated Head Space	Passive Headspace Concentration (charcoal strip)
Sludge	Coleman		Light Petroleum Distillate
C1	Bottle		Light - Medium Petroleum
C1	Table (Wood)		Light Petroleum Distillate
C1	Carpet & padding		Light Petroleum Distillate
C1	Flooring		Light Petroleum Distillate
C1	Trim		Negative
C2	Bottle		Light Petroleum Distillate
C2	Table (Wood)		Light Petroleum Distillate
C2	Carpet & padding		Light Petroleum Distillate
C2	Flooring		Light Petroleum Distillate
C2	Trim		Light Petroleum Distillate
C3	Bottle /table		Light Petroleum Product
C3	Carpet & padding		Light Petroleum Distillate
C4	Bottle		Light Petroleum Distillate
C4	Carpet & padding		Light Petroleum Distillate
C4	Table (wood)		Light Petroleum Distillate
Sludge	diethyl ether	di-ethyl ether, LPP	Light Petroleum Product
E1	Bottle	di-ethyl ether, LPP	di-ethyl ether, LPP
E1	Carpet & padding	di-ethyl ether, LPP	di-ethyl ether, LPP
E1	Trim	di-ethyl ether, LPP	di-ethyl ether, LPP
E1	Table (Wood)	di-ethyl ether, LPP	di-ethyl ether, LPP
E2	Bottle	di-ethyl ether, LPP	Light Petroleum Product
E2	Carpet & padding	di-ethyl ether, LPP	di-ethyl ether, LPP
E2	Table (Wood)	di-ethyl ether, LPP	di-ethyl ether, LPP
E3	Bottle area of table	Negative	Light Petroleum Product
E3	Carpet & padding	Negative	Negative
E3	Table (Wood)	Light Petroleum Product	Light Petroleum Product
E4	Bottle	di-ethyl ether, LPP	Light Petroleum Product
E4	Carpet & padding	di-ethyl ether, LPP	Light Petroleum Product
E4	Table (Wood)	Light Petroleum Product	Light Petroleum Product

Drug Analysis- OSU results

Upon LC-MS-MS analysis, each calibrator was used to generate a calibration curve based on a ratio of analyte peak area to internal standard peak area (quantitation or quant ratio). The methamphetamine and pseudoephedrine calibration curves are shown below in Figure 1 and Figure 2 respectively. Line equations for each curve are listed and the r-squared values for each calibration curve are at 0.999. If the quant ratio for a sample was in between the lowest and highest calibrator, the sample concentration was estimated using a best fit line of the calibration curve. The sample was deemed positive and the quantitated value is listed in parenthesis as a ng/mL concentration. If the quant ratio for a sample was below the lowest calibrator, but higher than five multiples of the negative control, that sample was positive, but could not be accurately quantitated. Any sample in this category was deemed "trace." Any sample with quant ratio less than five multiples of the negative control was reported as "negative." Many fire debris evidence samples were positive for methamphetamine and pseudoephedrine analytes. The results for each sample are listed in Table 3 below. All the data in Table 3 was obtained using samples diluted in running buffer, and if the samples were run at less dilution it is likely that most, if not all, would have been qualitatively positive for pseudoephedrine and methamphetamine. It should be noted that more concentrated samples should only be run after the diluted samples have proven negative as undiluted specimens might saturate the instrument and cause contamination issues.

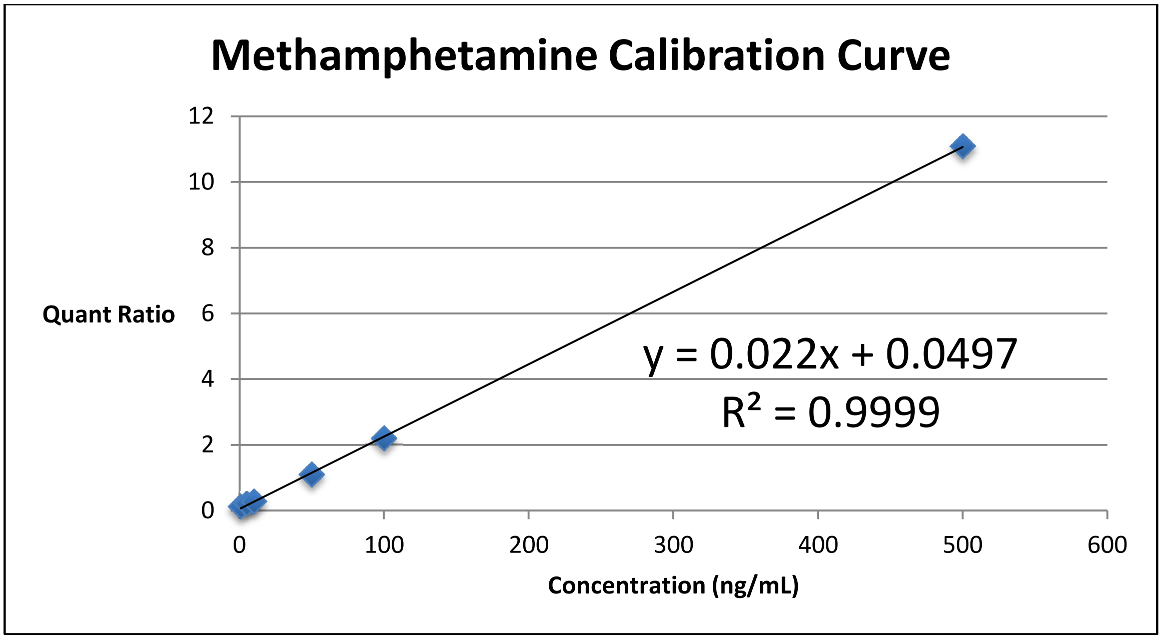

Figure 6. Methamphetamine Calibration Curve. Calibrators were plotted on a graph of concentration versus quantitation ratio. A "best fit" line was generated. The line equation containing slope and y-intercept is listed as well as the r-squared value.

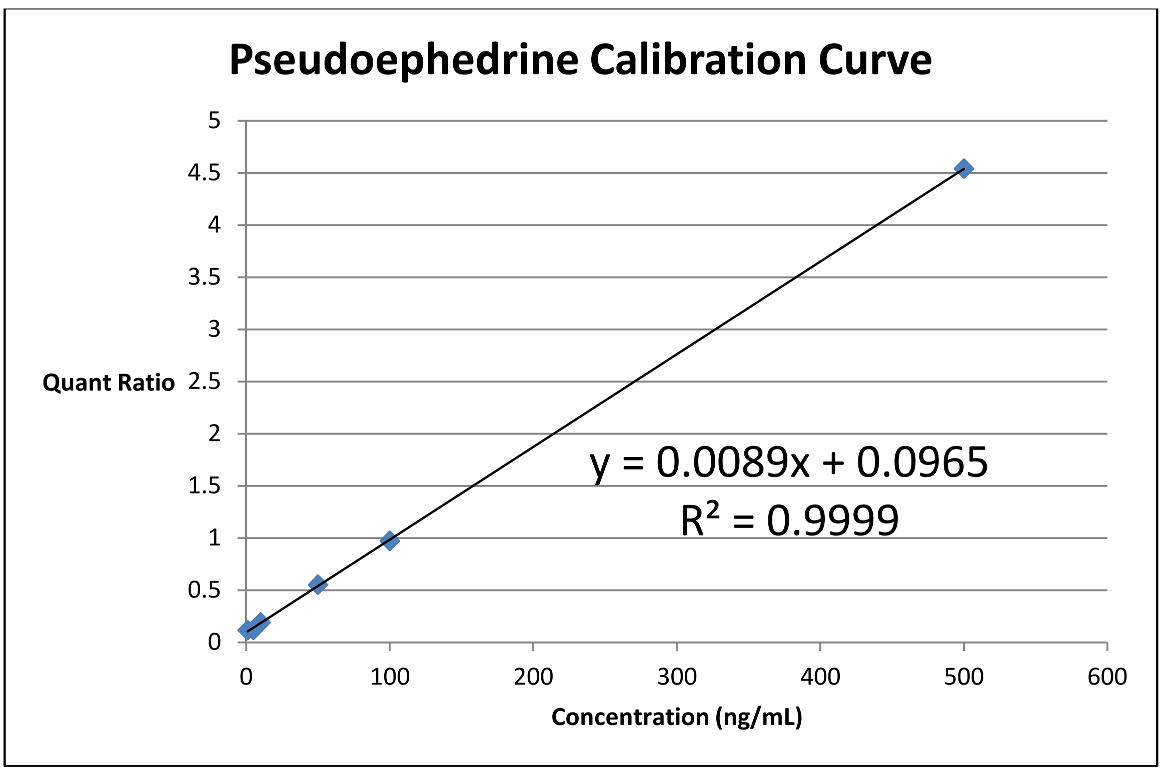

Figure 7. Pseudoephedrine Calibration Curve. Calibrators were plotted on a graph of concentration versus quantitation ratio. A "best fit" line was generated. The line equation containing slope and y-intercept is listed as well as the r-squared value.

Table 3. Drug Analysis Results (OSU). Each sample is organized according to fire experiment and sample type. Methamphetamine and pseudoephedrine results are listed in separate columns. A number in parenthesis represents an estimated concentration in ng/mL. Trace indicates that the drug was present, but at a ratio below the lowest calibrator. Negative indicates that no drug was found in the sample.

Experiment	Sample Collected	Methamphetamine Result	Pseudoephedrine Result
E1	Sludge	Positive (6.0)	Positive (49)
	Wall Wipe	Positive (76)	Positive (341)
	Wood	Trace*	Positive (54)
	Carpet	Positive (17)	Trace*
E2	Sludge	Positive (6.0)	Positive (48)
	Wall Wipe	Positive (11)	Positive (73)
	Wood	Positive (14)	Positive (100)
	Carpet	Trace*	Positive (27)
E3	Sludge	Negative	Trace*
	Wood	Negative	Negative
	Carpet	Negative	Negative
E4	Sludge	Positive (7.5)	Positive (67)
	Wood	Trace*	Positive (27)
	Carpet	Negative	Negative
C1	Sludge	Positive (7.8)	Positive (110)
	Wall Wipe	Positive (37)	Positive (332)
	Wood	Positive (42)	Positive (314)
	Carpet	Negative	Trace*
C2	Sludge	Negative	Positive (15)
	Wall Wipe	Positive (64)	Positive (478)
	Wood	Trace*	Positive (119)
	Carpet	Positive (53)	Positive (224)
C3	Sludge	Negative	Positive (22)
	Wood	Negative	Trace*
	Carpet	Negative	Negative
C4	Sludge	Trace*	Positive (53)
	Wood	Positive (22)	Positive (134)
	Carpet	Negative	Negative

Drug Analysis- TPD and OSBI results

Upon GC-MS analysis of E1 carbon disulfide samples at the Tulsa Police Department Forensic Laboratory, methamphetamine was detected in the bottle sample used during headspace analysis at FRL. No drugs were found in carbon disulfide from wood and carpet samples. Upon analysis of carbon strips from the FRL, methamphetamine and pseudoephedrine were detected in the bottle sample. No drugs were detected in the carbon strips from the wood or carpet samples.

At the Oklahoma State Bureau of Investigation, methamphetamine was detected by GC-MS analysis of the E2 carbon strip samples of the bottle. Analysis of actual fire debris samples from E2 detected methamphetamine in the bottle and wood samples. No drugs were detected in carpet samples.

CHAPTER V

CONCLUSIONS

Results Discussion

The results from the ATF's Fire Research Laboratory proved that arson analysis was successful in detecting ignitable residues from simulated clandestine methamphetamine laboratories. An ignitable liquid consistent with the methamphetamine cooks, either diethyl ether or Coleman fuel, was detected in every sample except C1 trim and E3 carpet/pad. Although these compounds have been detected many times prior in other scenarios, it was important to establish a successful arson analysis for this research project related to clandestine laboratories.

The results from the OSU Forensic Toxicology and Trace Laboratory indicated a multitude of positive samples for both methamphetamine and pseudoephedrine. Every fire experiment contained at least one drug detected, and some experiments had as many as 8 drug detections when combining all sample types. For example, E1 and E2 demonstrated a positive or trace result for methamphetamine and pseudoephedrine in every sample type. E3, on the other hand, only showed a positive pseudoephedrine result in the sludge sample. All other sample types were negative. This is comparable to the FRL results and the difficulty in detecting an ignitable liquid in the E3 carpet sample. E3-E4 and C3-C4 had a long burning duration than the others; therefore it was hypothesized that these samples would contain a less concentrated amount of drugs. According to Table 3 above, this trend is true. With more positive detections in experiments E1-E2 and C1-C2, it is clear that more burning time is directly related to elimination of drug molecules present.

When comparing sample types, the wipe samples were the most successful in positive drug detection. However, wipe samples were only collected in the short burn durations (E1-E2, C1-C2) because the walls in the remaining fire experiments were too severely damaged. The sludge and wood sample types were also successful as many resulted in detected methamphetamine and pseudoephedrine ions. Carpet samples were the least successful, with only 25% of samples resulting in detected methamphetamine and 50% having detected pseudoephedrine. Although the sample size is small, the results indicate the most desirable sample types in a methamphetamine lab fire. Providing investigators with this information will assist them in sample collection.

According to the results obtained from the TPD and OSBI crime laboratories, methamphetamine detection is possible with GC/MS. Additionally, it was proven that previously tested samples from arson analysis can be used to detect drugs as well. This is beneficial for arson investigations, especially when valuable samples are limited. Positive drug detection also proves that crime laboratories have the capability using their current instrumentation.

Conclusion

One-pot methamphetamine products were used to recreate fires in a residential environment. Fire debris samples of various types were collected and analyzed for ignitable liquids, which is standard for arson investigations. After positive accelerant detections from every fire recreation, the fire debris evidence was analyzed for methamphetamine and pseudoephedrine. Upon revisiting the research questions, the results proved that methamphetamine and pseudoephedrine detection is achievable in fire debris. The successful detection of the drugs of interest was performed on both LC-MS-MS and GC-MS instrumentation. In two situations, OSU and OSBI, the actual fire debris evidence samples were analyzed. Samples from the arson analysis were examined as well. TPD and OSBI were successful in detecting methamphetamine using the carbon disulfide and carbon strip samples from the Fire Research Laboratory. Cumulatively, the fire debris analysis at two local forensic laboratories demonstrated that methamphetamine detection can be implemented and that a single fire debris sample can be used for both arson and drug analysis.

This novel and ground-breaking research will provide a new tool for arson investigations. Although a positive methamphetamine result from fire debris evidence does not guarantee manufacturing of a controlled dangerous substance, it will strengthen the investigation and become a helpful addition to a first degree arson charge. Further research and testing of One-pot methamphetamine fires will lead to improved detection and understanding. Implementation of this new detection technique has the ability to keep criminals away from innocent people in the community for a long period of time, with steeper arson penalties. As an indirect result, this may dissuade individuals to manufacture methamphetamine within residences.

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VITA

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