Analysis of Lubricants at Trace Levels Using Infrared Spectroscopy

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ANALYSIS OF LUBRICANTS AT TRACE LEVELS USING INFRARED SPECTROSCOPY

by

TANMAI BANDARUPALLI

A thesis submitted in partial fulfillment of the requirements for the Honors Undergraduate Thesis in the Department of Chemistry in the College of Sciences and in the Burnett Honors College at the University of Central Florida

Orlando, Florida

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Thesis Chair: Dr. Candice Bridge
Abstract

Analysis of trace evidence involved in sexual assault investigations holds considerable potential as a newer avenue of identification when bulk, larger evidence is not found or unreliable. Trace analysis of forensic materials involves common findings such as strands of hair, residues left on clothing, shards of paint or glass, etc. In recent research focused on the analysis of trace materials found as evidence in a sexual assault, there has been promise in condom and bottled lubricant classification based on their chemical profiles that can provide an associative link in an investigation. Few studies have considered the examination of lubricant evidence at a trace level as it may be found on a crime scene or a victim. In this study, a new protocol will be tested and established to analyze trace lubricant evidence recovered from a fabric substrate, such as underwear, after sexual assaults using Fourier transform infrared (FTIR) spectroscopy. An experiment is proposed to examine the comparison of the spectra resulting from FTIR spectroscopic analysis of bulk and trace level lubricants recovered from a cotton substrate. The resulting spectra will be compared for their similarities using multivariate statistical techniques to test the viability of the approach.
Acknowledgements

I would like to firstly thank my committee chair, Dr. Candice Bridge who not only introduced me to Forensic Chemistry and helped me become successful in an analytical chemistry lab as a Biomedical Sciences major, but also supported me throughout the Honors Undergraduate Thesis program.

Thank you to Dr. Santana Thomas for helping me throughout my time in this lab and answering my many questions.

I would also like to thank Dr. Jack Ballantyne and Dr. Denisia Popolan-Vaida for agreeing to be on my committee and providing me with helpful feedback and suggestions.
# Table of Contents

1. Introduction

2. Research Design
   I. Preparation of Stock Solution
   II. Preliminary Study
   III. Time-Dependent Studies
   IV. FTIR

3. Results and Discussion
   I. Preliminary Study
   II. Time-Dependent Study 1
   III. Time-Dependent Study 2
   IV. Time-Dependent Study 3

4. Conclusion

5. Future Work

6. References
List of Figures

FIGURE 2.1: CALCULATION OF 1000 PPM LUBRICANT STOCK SOLUTIONS........................................5

FIGURE 2.2: THE JASCO 6600 SERIES FTIR INSTRUMENT .............................................................9

FIGURE 3.1: PCC DATA ANALYSIS FOR SILIQUID SILVER (PDMS) SAMPLES OF PRELIMINARY STUDY ..........................................................................................................................11

FIGURE 3.2: PCC DATA ANALYSIS FOR ASTROGLIDE (PEG) SAMPLES OF PRELIMINARY STUDY .....11

FIGURE 3.3: AVERAGE PCC SCORES OF EXTRACTION SOLVENTS VS. LUBRICANT TYPES [14] ..........12

FIGURE 3.4: OVERLAIN SPECTRA CHART OF PEG SAMPLES IN THE PRELIMINARY STUDY.............13

FIGURE 3.5: PCC DATA ANALYSIS FOR SILIQUID SILVER (PDMS) SAMPLES OF TIME-DEPENDENT STUDY 1 .....................................................................................................................................15

FIGURE 3.6: PCC DATA ANALYSIS FOR ASTROGLIDE (PEG) SAMPLES OF TIME-DEPENDENT STUDY 1 .....................................................................................................................................15

FIGURE 3.7: OVERLAIN FTIR SPECTRA OF PDMS LUBRICANT IN TIME-DEPENDENT STUDY 1 ....16

FIGURE 3.8: OVERLAIN SPECTRA OF PEG TIME-DEPENDENT STUDY 1............................................17

FIGURE 3.9: PCC DATA ANALYSIS FOR FLAVORED PDMS LUBRICANT SAMPLES OF TIME-DEPENDENT STUDY 2 ........................................................................................................19

FIGURE 3.10: PCC DATA ANALYSIS FOR FLAVORED PEG LUBRICANT SAMPLES OF TIME-DEPENDENT STUDY 2 ........................................................................................................19

FIGURE 3.11: OVERLAIN SPECTRA OF PDMS LUBRICANT IN TIME-DEPENDENT STUDY 2...........20
Figure 3.12: PCC Data Analysis for Anesthetic PDMS Lubricant Samples of Time-Dependent Study 3 ........................................................................................................................................ 23

Figure 3.13: PCC Data Analysis for Anesthetic PEG Lubricant Samples of Time-Dependent Study 3 ........................................................................................................................................ 23

Figure 3.14: Average Correlation Trends of PDMS Anesthetic Samples Compared to Neat and 0 min Samples ........................................................................................................................................ 24
List of Tables

**Table 2.1:** Lubricant Type and Time Intervals for Time-Dependent Studies Conducted 8

**Table 3.1:** Averages and Standard Deviations of Correlations between PDMS Trace Samples to Neat Lubricants in Time-Dependent Study 2 ................................................................. 21

**Table 3.2:** Averages and Standard Deviations of Correlations between PDMS Trace Samples to 0-Minute Trace Samples in Time-Dependent Study 2 ................................................. 21

**Table 3.3:** Statistical Analysis of the Correlation Trends between PDMS Trace Lubricants and Neat Lubricant Samples .......................................................................................... 22

**Table 3.4:** Averages and Standard Deviations of Correlations between PEG Trace Samples to Neat Lubricants in Time-Dependent Study 3 .......................................................... 25

**Table 4.1:** Times Where Each Trace Lubricant Type Has a Moderate Correlation (~0.70) with the Pure Neat Lubricants .......................................................................................... 27
1. Introduction

Cases of sexual assaults are alarmingly prominent in modern society with approximately 43% of women and 25% of men experiencing some form of contact sexual violence in their lifetimes [1]. The prevalence of sexual offenses and the consistent difficulty in identifying the perpetrator during an investigation lends to the importance of research towards a newer forensic analytical approach. With the steady increase in sexual assault cases where no DNA evidence is recovered, focus is placed on an alternative, non-DNA type of evidence that can be found on the scene or the victim, which could be beneficial to the investigation [2]. Whether it be the desire to prevent the spread of sexually transmitted diseases or the hope to avoid leaving a DNA profile behind, sexual offenders now commonly wear condoms [2]. This precaution, in many cases, prevents the retrieval and analysis of large amounts of biological evidence, such as seminal fluids, that can produce a more definitive link to potential suspect(s) through DNA identification. However, in these instances of condom use, trace evidence such as lubricant residue from the condom can be retrieved and analyzed as evidence in an investigation. In a 1996 study, Blackledge emphasizes that there is a multitude of information that can be gathered from lubricant residue analysis including corpus delicti, evidence of penetration, associative evidence, and the ability to link acts of serial rapists [2]. Considering the multiple purposes that analysis of trace forensic material may provide, it is apparent that it can be quite useful in gathering information during a sexual assault investigation.

The analysis of trace material in chemistry involves the examination of very small amounts of elements and compounds—microconstituents [3]. Trace constituents, in the past, were those considered to be present but in amounts so small that they were thought to make no significant contribution to a conclusion [3]. With more advances in analytical techniques, the definitions of
trace constituents have become more flexible and spectroscopic technologies have opened the possibility of measuring these elements precisely and identifying their characteristics [4]. For instance, in a 1994 study by Blackledge, FTIR spectroscopy techniques were utilized to identify traces of polydimethylsiloxane lubricants from latex condoms in cases of sexual assault [5]. The protocols established in that study have set a precedence to the trace lubricant analysis we continue to find new approaches with today. One of these recent new approaches is shown in a 2019 study by Kapgate where FTIR spectroscopic techniques were successfully used to characterize condom brand spectrum patterns in efforts to explore trace contact evidence in sexual assaults as we plan to do in this study [6]. Kapgate’s results were able to offer unique forensic intelligence during sexual assault investigations [6]. The ability to retrieve and analyze trace evidence is a valuable approach in forensic science because of its capacity to associate small amounts of evidence to larger, more identifiable pieces. The connection established provides a link based on evidence from material that would otherwise be ignored because of its sparsity and/or lack of research in the community.

Condoms are usually coated with silicone-based lubricant and are the most common source of trace lubricant residue within a sexual assault case that may contain little to no DNA evidence [7]. However, other types of sexual lubricants were observed within sexual investigations and should be considered in analysis as well [7]. Examining components of various types of lubricant sources such as: water-based lubricants, silicone-based lubricants, oil-based lubricants, etc. allows for more specificity in the identification of lubricant evidence by providing a greater range of classification. In the chemical analysis of condoms lubricants, it is seen that common components include polydimethylsiloxane (PDMS), polyethylene glycol (PEG), and propylene (PG) among others [7]. In addition, their components vary by the chemical differences that arise from additives in the lubricants such as flavors and anesthetics. Using these recognized differences in chemical
components between lubricants among others, a 2018 study by Baumgarten, Maric, et al. identified 11 classes of silicone-based lubricant using Direct Analysis in Real Time-Mass Spectrometry (DART-MS) [8]. Their analysis of 37 silicone-based personal and condom lubricants produced a range of spectra that were able to identify the major components determining a chemical fingerprint that allowed for identification of lubricants beyond the basic division of water and silicone-based [8]. silicone-based lubricants, condoms and bottled, are one of the main lubricants marketed around the world so this study was able to establish sections of classification for a large set of lubricants [8]. The success of this study, as well as others regarding the chemical composition of condoms, indicates that lubricant evidence can be effectively analyzed using spectroscopic techniques and classified with the data produced from them; a goal that the study proposed will be aiming for with the analysis of lubricant evidence at a trace level.

The spectroscopic techniques that will be used to analyze trace lubricant residue with the aim of classification in this study will be with the FTIR instrument. Using the FTIR instrument’s sensitivity to recognize molecular components, frequencies are able to record specific structural characteristics of the material being analyzed [9]. In addition to the Blackledge and Kapgate studies mentioned previously, many researchers have had success with FTIR spectroscopic techniques to analyze trace lubricant evidence. A study by Cho and Huang in 2012 used FTIR spectroscopic techniques to identify major components of condom lubricants and their frequency in the market using spectral region analysis [10]. Further, the study stated that the FTIR instrument had shown to be useful both in analyzing condoms as well as trace evidence and had allowed the researchers to create a database of IR spectra of condoms to establish in the Central Police University [10]. FTIR spectroscopy has become a fixture in the established routine of analyzing common evidence from sexual assault investigations such as evidence swabs retrieved from the scene or victim [10]. In a
more recent 2020 study by Burnier, FTIR spectroscopy was discussed to offer better spectral quality in trace lubricant component identification because of its ability to analyze trace extracts, its ability to recognize small differences among PEG lubricants, etc. [11] In this study, we will deposit trace levels of lubricant residue onto a fabric substrate as it may be found from a sexual assault and then extract that lubricant into a solution in which it may be analyzed on the FTIR instrument. Analysis of highly concentrated solutions of lubricants will also be performed on the FTIR. Both the diluted and concentrated samples (trace and bulk) will undergo multivariate statistical analysis to determine the association that can be made after extraction of lubricant from a fabric.

Essentially, the identification of trace lubricant evidence that is recovered from a crime should undergo an established protocol that has been tested for its accuracy. Sexual lubricant analysis is an emerging field in trace analysis and thus studies are conducted to validate it as evidence.

The objective of this study is to exhibit the viability of utilizing the FTIR as a screening tool to identify and classify trace lubricant evidence based on its chemical components when extracted from a fabric substrate. This study can be applied to sexual assault investigations in the analysis of lubricant residue retrieved from cotton fabric such as sheets and/or clothing. Due to the diverse nature of sexual lubricants that can be found in sexual assault cases, this study incorporates a diverse collection of sexual lubricants inclusive of brands, types, additives, and marketing categories.
2. Research Design

I. Preparation of Stock Solution

For each of the studies conducted (e.g., preliminary and time-dependent), 1000 parts per million (ppm) stock solutions were prepared from the lubricants using a 50/50 mixture of dichloromethane/methanol (DCM/MeOH) solvent according to the calculations below.

\[
1000 \text{ ppm} = \frac{4 \text{ uL solute}}{4000 \text{ uL solution}}
\]

\[
4000 \text{ uL solution} = 4 \text{ uL solute} + 3996 \text{ uL solvent}
\]

Figure 2.1: Calculation of 1000 ppm lubricant stock solutions

Based on these calculations, stock solutions were prepared by measuring 4 uL of sample lubricant with a micropipette and combining it with 3996 uL of the dichloromethane/methanol solvent. A DCM/MeOH solvent was used throughout this study with the aim of increasing the number of components of the lubricants that will be extracted into the solvent. This is because the polarities of dichloromethane and methanol differ and since similar polarities dissolve each other, the mixture of two solvents is expected to dissolve more components from the lubricant than just either one alone (i.e., polar or non-polar. The stock solution was then vortexed and chilled for continual use.

II. Preliminary Study

A preliminary study was conducted with varying volumes of prepared stock solution in order to determine the optimal amount to be utilized in the time-dependent experiments of the study. In the preliminary study, a regular bottled polydimethylsiloxane (PDMS) lubricant and a regular bottled
polyethylene glycol (PEG) lubricant void of any additives were used. Sliquid Silver was used for the PDMS lubricant and Astroglide was used for the PEG lubricant. 1000 ppm stock solutions were prepared for both the lubricants in accordance to the calculations in Figure 2.1.

Pieces of cotton fabric from women’s underwear were measured and cut to the dimensions of 1 inch by 1 inch for samples to be extracted from. Using the 1000 ppm stock solution, volumes of 25 $\mu$L, 50 $\mu$L, 100 $\mu$L, 500 $\mu$L, and 1000 $\mu$L were deposited onto five different pieces of cotton to test the level of viable results attained from analyzing at each of the trace levels on the FTIR instrument. All volumes were delivered onto a cotton substrate using a micropipette and the 500 $\mu$L and 1000 $\mu$L measurements were delivered onto the fabric in increments of 100 $\mu$L that were allowed to dry each time as to not oversaturate the fabric all at once with large volumes. Following the preparation of each of the cotton fabrics with their respective amounts of lubricant solution, the cotton was deposited into a vial of 1700 $\mu$L solution of DCM/MeOH for extraction. The fabric was vortexed in this solvent and the cotton fabric was then removed from the vial, leaving a solution of DCM/MeOH and an extracted trace amount of lubricant recovered from the cotton substrate. Small amounts of the extracted solution were then prepared to be analyzed on the FTIR instrument shown in Figure 2.2 with the varying volumes of deposited stock solution being the differing factor in each of the samples. This procedure was done in a similar fashion for both the PEG and PDMS lubricant being tested.

III. Time-Dependent Studies

Following analysis of the spectra and results of the preliminary study as discussed in more detail in the next section, it was decided that depositing a 1000 $\mu$L volume of stock solution onto cotton fabric as a constant during the time-dependent study was the lowest volume that would yield
reliable results. In the time-dependent studies, a 1000 uL deposited volume was consistently used while the time the lubricant solution was allowed to dry on each cotton fabric was altered as a variable. In the first experiment, trace stock solutions of both regular bottled PDMS lubricant and regular bottled PEG lubricant with no additives, Sliquid Silver and Astroglide respectively, were deposited onto a cotton fabric and allowed to dry for five different time lengths: 0-minute, thirty (30) minutes, two (2) hours, three (3) hours, and twenty-four (24) hours. By allowing the samples to dry for various specified amounts of time, the study takes into account any evaporation of components of the lubricant and trends of degradation as it may naturally occur after being recovered from a crime scene when the time the evidence was sitting in the crime scene is known or even unknown. This allows the model of the lab-made trace evidence to emulate forensic material when analyzed for components.

Each of the cotton fabric pieces, following their allocated drying time, were then placed into a vial with dichloromethane/methanol solvent and vortexed to promote extraction of the sexual lubricant from the fabric and into the solution. A neat sample, the lubricant sample without solvent, was used to analyze each commercial lubricant as bulk evidence without any lab-induced alterations. The chemical profile of the pure commercial lubricant was attained by the FTIR without any other substance interference. In addition, the two prepared aforementioned controls (a solvent control and negative control) were also analyzed on the FTIR.

After analysis of the Time-Dependent Study 1 spectra data, it was decided that more time intervals should be added to the future time-dependent experiments for broader degradation data. For Time-Dependent Study 2, trace stock solutions of flavored PDMS lubricant, Doc Johnson Drip Spicy, and flavored PEG lubricant, JO H2O Tangerine Dream, were deposited onto a cotton fabric
in a similar fashion and allowed to dry for eight different time lengths: 0-minute, thirty (30) minutes, one (1) hour, two (2) hours, three (3) hours, and twenty-four (24) hours, forty-eight (48) hours, and seventy-two (72) hours. In Time-Dependent Study 3, the same drying time intervals were studied for a PDMS lubricant with an anesthetic additive, Pjur Original Backdoor Silicone, and a PEG lubricant with anesthetic additive, Crazy Girl Anal Ease Desensitizing Gel. A comprehensive view of the time intervals and lubricants used for each of the studies can be seen in Table 2.1.

Table 2.1: Lubricant Type and Time Intervals for Time-Dependent Studies conducted

<table>
<thead>
<tr>
<th>Time-Dependent Study 1</th>
<th>Time-Dependent Study 2</th>
<th>Time-Dependent Study 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMS Lubricant w/ no Additives</td>
<td>PDMS Lubricant w/ Flavoring Additive</td>
<td>PDMS Lubricant w/ Anesthetic Additives</td>
</tr>
<tr>
<td>PEG Lubricant w/ no Additives</td>
<td>PEG Lubricant w/ Flavoring Additive</td>
<td>PEG Lubricant w/ Anesthetic Additives</td>
</tr>
<tr>
<td>0 min</td>
<td>0 min</td>
<td>0 min</td>
</tr>
<tr>
<td>30 min</td>
<td>30 min</td>
<td>30 min</td>
</tr>
<tr>
<td>2 hours</td>
<td>2 hours</td>
<td>1 hour</td>
</tr>
<tr>
<td>3 hours</td>
<td>3 hours</td>
<td>2 hours</td>
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<tr>
<td>24 hours</td>
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<tr>
<td>24 hours</td>
<td>24 hours</td>
<td>2 hours</td>
</tr>
<tr>
<td>48 hours</td>
<td>48 hours</td>
<td>3 hours</td>
</tr>
<tr>
<td>72 hours</td>
<td>72 hours</td>
<td>3 hours</td>
</tr>
</tbody>
</table>

IV. FTIR

The prepared samples were then analyzed on the Jasco 6600 Series FTIR instrument shown in Figure 2.2 in three replicates for each sample. Each extract was analyzed on the FTIR as well as neat samples, negative controls, and solvents to establish a set of spectra of all the substances being utilized in the study. An instrument blank (air background) was taken before each run to identify any contaminant that may be present while nothing is on the crystal where samples were being
deposited. The air background was then subtracted from each reading of the sample spectrum generated. Following each run, the crystal was cleaned with both a non-polar and polar solvent (hexane and methanol) before introducing the next sample in order to ensure no contaminant components are in the next reading. Two 5 uL of the extracted samples were deposited onto the crystal using a micropipette and allowed to dry to form a lubricant film for an FTIR reading. All spectra were obtained after undergoing background subtraction, attenuated total reflectance (ATR), and baseline correction for each replicate.

Figure 2.2: The Jasco 6600 Series FTIR Instrument
3. Results and Discussion

I. Preliminary Study

The data retrieved from the FTIR spectra for the preliminary study was studied in a more qualitative sense through overlaying spectra and observing similarities and differences as well as quantitatively through the Pearson Correlation Coefficient (PCC) multivariate analysis technique. PCC analysis is useful in comparing the similarity or association between two variables with continuous data sets with -1 or 1 being the most correlated, inversely and directly respectively, and 0 indicating no relationship present [14]. PCC multivariate analysis was used in this study to compare the data from the spectra of the trace samples to the spectra data of the pure lubricant samples as well as the trace samples to each other. On the following page, in Figure 3.1, the PCC data for the PDMS lubricant analyzed in the preliminary study can be observed. In Figure 3.2, the PCC data for the PEG lubricant analyzed in the preliminary study can be observed.
11

Figure 3.1: PCC Data Analysis for Sliquid Silver (PDMS) Samples of Preliminary Study

Figure 3.2: PCC Data Analysis for Astroglide (PEG) Samples of Preliminary Study
Using the established research from a 2021 study by Thomas, we can refer to the average PCC scores that should be expected from each type of lubricant extracted in each type of solvent [15]. In Figure 3.3, we are able to observe a compiled version of these conclusions that can be used for analysis of our data.

<table>
<thead>
<tr>
<th>Lubricant-type</th>
<th>Neat vs MeOH</th>
<th>Neat vs Hexane</th>
<th>Neat vs DCM/MeOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil</td>
<td>0.34 ± 0.01</td>
<td>−0.05 ± 0.01</td>
<td>0.84 ± 0.02</td>
</tr>
<tr>
<td>Water</td>
<td>0.65 ± 0.02</td>
<td>−0.15 ± 0.02</td>
<td>0.66 ± 0.04</td>
</tr>
<tr>
<td>Silicone</td>
<td>0.55 ± 0.03</td>
<td>0.89 ± 0.01</td>
<td>0.80 ± 0.01</td>
</tr>
</tbody>
</table>

Figure 3.3: Average PCC scores of extraction solvents vs. lubricant types [15]

From this research, a PCC score around 0.80 with a deviation of around 0.01 should be observed for the PDMS lubricant in the DCM/MeOH solvent being utilized in this study.

In Figure 3.1, it can be observed that the PCC scores showed a general increasing trend of correlation as more lubricant volume was deposited onto the cotton for extraction. Observing the first three rows of data that compared the various samples to the pure neat sample, the correlation coefficient between the 25 $\mu$L and the neat in all the replicates fell in the 0.3 to 0.4 range. As a comparison, the 500 $\mu$L sample’s correlation to the neat sample yielded coefficients between 0.58 and 0.7 in all the replicates. These PCC scores, however, were still not the average expected to be seen as derived from the conclusions made in Figure 3.3. The expected average PCC score of 0.8 was finally observed in the three replicates of the 1000 $\mu$L volume samples, allowing the conclusion to be made that a 1000 $\mu$L deposition of lubricant solution is the best to move forward with for the PDMS lubricant samples in the time-dependent studies.

In Figure 3.2, a similar general increase was observed in the PCC scores of the PEG lubricant samples as compared to the neat lubricants. There were a few notable dips, though, in two of the
500 uL sample replicates as well as the first replicate of the 1000 uL sample. In order to observe which chemical components may be causing the inconsistency, an overlain chart seen in Figure 3.4 was created with the spectra of the pure neat lubricant, the DCM/MeOH solvent, two sample replicates which produced low correlation scores, and a sample replicate that produced a consistent correlation with the trend. It can be observed that the inconsistencies are readily seen between the 3000 and 3500 wavelengths where there is a notable hydroxy (-OH) peak that was inherent to both the solvent and the water-based lubricant. Replicate spectra with lower correlation coefficients, 500uL_W0001_2 and 1000uL_W0001_1, were seen to have smaller -OH peaks, leading to the conclusion the solvent may have properly evaporated from the sample on the IR prior to analysis in some of the samples but not all. This drying time allowed the methanol to evaporate which caused some evaporation of the -OH components.

![Overlain Spectra of PEG Samples in Preliminary Study](image)

Figure 3.4: Overlain spectra chart of PEG Samples in the Preliminary Study
To determine the best volume of PEG lubricant stock solution to move forward with as a constant in the time-dependent studies, we may again refer to Figure 3.2 which expects an average PCC score of 0.66 with 0.04 deviation in DCM/MeOH solvent. The largest correlation coefficient, 0.68, is observed at the 1000 \( \mu L \) volume sample so due to some of the dips and inconsistencies it was decided that it was best so safely decide on the largest volume, 1000 \( \mu L \) for the PEG lubricants as well in the time-dependent studies.

II. Time-Dependent Study 1

In Time-Dependent Study 1, a 1000 \( \mu L \) volume deposition of the 1000 ppm trace lubricant stock solution onto the cotton fabric posed as a constant variable. The independent variable changed in this study was the time that the deposed sample was allowed to dry on the cotton fabric before it was extracted for analysis. A PCC analysis was again conducted for the data produced by the PDMS, Sliquid Silver, and PEG, Astroglide, lubricants used in this study as shown in Figures 3.5 and 3.6 respectively on the following page.

Studying the PCC scores of the PDMS lubricant comparisons in Figure 3.5, as hypothesized, the correlation of the trace sample to the neat sample is highest when the lubricant is extracted into solvent immediately after the cotton sample is created as opposed to after it is let out to dry for some time. There is a steady decrease in the correlation coefficients as the samples lose more chemical components likely due to evaporation. We can see this with the 0-minute drying time samples having correlations between 0.8 and 0.9 in comparison to the neat sample while the 24-hour drying time samples have correlations between 0.6 and 0.8.
Figure 3.5: PCC Data Analysis for Sliquid Silver (PDMS) Samples of Time-Dependent Study 1

Figure 3.6: PCC Data Analysis for Astroglide (PEG) Samples of Time-Dependent Study 1
In the data in Figure 3.5, we do observe a sharp dip in correlation, however, in the second replicate of the 2-hour sample that is inconsistent with the remainder of the PCC scores. Because the inconsistency is present in one replication rather than all the replications of the 2-hour sample, we were aware that the error occurred during IR analysis. To examine this possibility, a chart of overlain spectra of the inconsistent sample replication, the neat sample, and the DCM/MeOH solvent were compared in Figure 3.7.

![Overlain FTIR Spectra for PDMS Time Study 1](image)

**Figure 3.7: Overlain FTIR spectra of PDMS Lubricant in Time-Dependent Study 1**

From the spectra seen in Figure 3.7 we are able to observe that the 2-hour sample replicate we are concerned with has a very uncharacteristic peak in the -OH region that is quite similar to that inherent to the DCM/MeOH spectrum. Thus, it is fair to assume that the uncharacteristic peak of the sample likely arose from the FTIR instrument being operated to analyze the replicate before the solvent had finished drying. This sharp difference between the neat silicone sample with no peak
and the 2 hours sample with a large -OH peak explains the low dip in correlation in the PCC analysis.

Observing the PCC scores of the Astroglide PEG lubricant samples in Figure 3.6, we observe consistently high correlation between the trace samples and the neat lubricants throughout all the time intervals in the study. The uncharacteristic dips in a few of the replicates in the 0-minuet and 30-minute samples can again be explained by inconsistencies in FTIR sample drying times prior to analysis as shown in the spectra in Figure 3.8.

![Overlain Spectra of PEG Time Study 1](image)

**Figure 3.8: Overlain Spectra of PEG Time-Dependent Study 1**

The PCC scores, however, have little deviation even with the extensive drying time of 24 hours. This lack of deviation indicated that the chemical components in the PEG lubricant had little to no loss in 24 hours’ time and to obtain a better idea of the degradation trends of the PEG
lubricant, future time-dependent studies should have additional measures following drying times of 48 hours and 72 hours as well. This applies for the PDMS lubricant as well which had a fairly high correlation of approximately 0.6 at 24 hours. Additionally, a 1-hour sample was created to evaluate if the dips observed in the correlation at 0 minute and 30 minute can be explained by analysis error as predicted or if there were degradation trends at that point in time.

III. Time-Dependent Study 2

In Time-Dependent Study 2, the 1000 $\mu$L volume deposition was kept constant, and the independent variable was the changing time intervals of sample drying time before extraction and analysis. PCC calculations were again conducted for the data produced by the PDMS, Doc Johnson Drip Spicy, and PEG, JO H2O Tangerine Dream, lubricants used in this study as shown in Figures 3.9 and 3.10 respectively on the following page.

In Figure 3.9, we are able to observe an immediately apparent drop in correlation between the trace PDMS lubricant samples and the neat lubricant even after the 0-minute immediate extraction following sample creation. All three replicates of the 0-minute PDMS samples indicate the poor relationship to the pure lubricant with coefficients ranging between 0.3 and 0.4. This correlation steadily decreased even more as drying times increased with the final 72-hour drying time sample having correlations between 0.2 and 0.3 with the neat lubricant. In the overlain spectra graph below in Figure 3.11, it can be observed that not all of the chemical components in the neat sample are present in any of the trace lubricant extractions being tested.
Figure 3.9: PCC Data Analysis for Flavored PDMS Lubricant Samples of Time-Dependent Study 2

| Sample Name | PCC Data Value 1 | PCC Data Value 2 | PCC Data Value 3 | PCC Data Value 4 | PCC Data Value 5 | PCC Data Value 6 | PCC Data Value 7 | PCC Data Value 8 | PCC Data Value 9 | PCC Data Value 10 | PCC Data Value 11 | PCC Data Value 12 | PCC Data Value 13 | PCC Data Value 14 | PCC Data Value 15 | PCC Data Value 16 | PCC Data Value 17 | PCC Data Value 18 | PCC Data Value 19 | PCC Data Value 20 |
|-------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| Sample PDMS | 0.8964382057 PX  | 0.9981461286 PX  | 0.9403153813 PX  | 0.8970784647 PX  | 0.9103280524 PX  | 0.9852847878 PX  | 0.9825185486 PX  | 0.8574052474 PX  | 0.9063248362 PX  | 0.9502608598 PX  | 0.9373334064 PX  | 0.9542312328 PX  | 0.9063636777 PX  | 0.8957476723 PX  | 0.9284828267 PX  | 0.8868512939 PX  | 0.8575437818 PX  | 0.9735824526 PX  | 0.9910888678 PX  |
| Sample PDMS | 0.8964382057 PX  | 0.9981461286 PX  | 0.9403153813 PX  | 0.8970784647 PX  | 0.9103280524 PX  | 0.9852847878 PX  | 0.9825185486 PX  | 0.8574052474 PX  | 0.9063248362 PX  | 0.9502608598 PX  | 0.9373334064 PX  | 0.9542312328 PX  | 0.9063636777 PX  | 0.8957476723 PX  | 0.9284828267 PX  | 0.8868512939 PX  | 0.8575437818 PX  | 0.9735824526 PX  | 0.9910888678 PX  |

Figure 3.10: PCC Data Analysis for Flavored PEG Lubricant Samples of Time-Dependent Study 2

| Sample Name | PCC Data Value 1 | PCC Data Value 2 | PCC Data Value 3 | PCC Data Value 4 | PCC Data Value 5 | PCC Data Value 6 | PCC Data Value 7 | PCC Data Value 8 | PCC Data Value 9 | PCC Data Value 10 | PCC Data Value 11 | PCC Data Value 12 | PCC Data Value 13 | PCC Data Value 14 | PCC Data Value 15 | PCC Data Value 16 | PCC Data Value 17 | PCC Data Value 18 | PCC Data Value 19 | PCC Data Value 20 |
|-------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| Sample PEG  | 0.8964382057 PX  | 0.9981461286 PX  | 0.9403153813 PX  | 0.8970784647 PX  | 0.9103280524 PX  | 0.9852847878 PX  | 0.9825185486 PX  | 0.8574052474 PX  | 0.9063248362 PX  | 0.9502608598 PX  | 0.9373334064 PX  | 0.9542312328 PX  | 0.9063636777 PX  | 0.8957476723 PX  | 0.9284828267 PX  | 0.8868512939 PX  | 0.8575437818 PX  | 0.9735824526 PX  | 0.9910888678 PX  |
| Sample PEG  | 0.8964382057 PX  | 0.9981461286 PX  | 0.9403153813 PX  | 0.8970784647 PX  | 0.9103280524 PX  | 0.9852847878 PX  | 0.9825185486 PX  | 0.8574052474 PX  | 0.9063248362 PX  | 0.9502608598 PX  | 0.9373334064 PX  | 0.9542312328 PX  | 0.9063636777 PX  | 0.8957476723 PX  | 0.9284828267 PX  | 0.8868512939 PX  | 0.8575437818 PX  | 0.9735824526 PX  | 0.9910888678 PX  |
The immediate but consistent poor correlation between the PDMS trace lubricant samples in Time-Dependent Study 2 and the neat lubricants are caused by the loss of the identifiable chemical components during sample preparation, before they were tested on the FTIR instrument. Because the drastically poor correlations did not exist for the PDMS lubricant with no additives in Time-Dependent Study 1, it can be inferred that the flavored chemical components in the Doc Johnson Spicy Drip used in this study were not able to dissolve in the DCM/MeOH solvent used for extraction and thus could not be caught on the FTIR instrument.

Table 3.1 shows the trace PDMS lubricant samples average correlations to the neat and the standard deviations and Table 3.2 shows the trace PDMS lubricant samples average correlation to the 0-minute replications’ analyzed data. From the calculations shown in Table 3.2, we are able to see that the samples are consistent and comparable between themselves even if they have poor
correlations to the neat. This shows that in a real crime lab application where 0-minute extractions are compared to rather than pure lubricants, this data could still be effective if the lubricants were to be extracted by a different, more non-polar, solvent.

Table 3.1: Averages and Standard Deviations of Correlations between PDMS trace samples to neat lubricants in Time-Dependent Study 2

| Table 3.2: Averages and Standard Deviations of Correlations between PDMS trace samples to 0-minute trace samples in Time-Dependent Study 2 |

In Figure 3.10, there is a contrasting trend to be observed where the correlation coefficients between the trace PEG lubricant samples and the neat lubricants consistently range from 0.9 to 1.0 even after the 72-hour drying time mark which had correlations of 0.97, 0.98, and 0.98 with the neat lubricant in the three replications analyzed. In these PEG lubricant samples with the flavoring additives, it can be understood that the chemical components have excellent retention in DCM/MeOH solvent and are not prone to degradation even after extensive drying time. An interesting facet to explore is if this extends to PEG flavored lubricants in a broad nature or just the JO H2O Tangerine Dream lubricant tested.

IV. Time-Dependent Study 3

In Time-Dependent Study 3, the 1000 μL volume deposition was kept constant, and the independent variable was the changing time intervals of sample drying time before extraction and
analysis. PCC calculations were again conducted for the data produced by the PDMS, Pjur original backdoor relaxing silicone, and PEG, Crazy Girl Anal Ease Desensitizing Gel, lubricants used in this study as shown in Figures 3.12 and 3.13 respectively on the following page.

In Figure 3.12, it can be observed that the PDMS lubricant with anesthetic analyzed here shows similar patterns of chemical component degradation as with the regular PDMS lubricant with no additives analyzed in Time-Dependent Study 1. After a 72-hour drying time, the anesthetic PDMS lubricants here are shown to still have a 0.6 to 0.7 correlation with the neat indicating that although some chemical components were lost, a generally high number of similarities were able to be established even following a 72-hour drying time. The sharp dip in correlations with the 48-hour sample can likely be explained by an error in the sample creation because of the consistent error in each of the sample’s replications. In order to get a quantitative and visual understanding of this error, a 95% confidence interval was generated for each of the correlation scores between the trace PDMS lubricant samples and the pure neat lubricants as shown in Table 3.3. A graph charting the trend of the correlations with error bars generated from the confidence intervals in Table 3.3 is shown in Figure 3.14.

Table 3.3: Statistical analysis of the correlation trends between PDMS trace lubricants and neat lubricant samples

<table>
<thead>
<tr>
<th>comparison to neat</th>
<th>Neat_50003_01</th>
<th>0min_50003_01</th>
<th>30min_50003_01</th>
<th>1hr_50003_01</th>
<th>2hrs_50003_01</th>
<th>3hrs_50003_01</th>
<th>4hrs_50003_01</th>
<th>48hrs_50003_01</th>
<th>72hrs_50003_01</th>
</tr>
</thead>
<tbody>
<tr>
<td>average</td>
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<td>0.69387022</td>
<td>0.546503123</td>
<td>0.60453935</td>
<td>0.60402881</td>
<td>0.564837077</td>
<td>0.645337077</td>
<td>0.08934284</td>
<td>0.6295516919</td>
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<tr>
<td>stdv</td>
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<td>0.026759248</td>
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<td>0.040845734</td>
<td>0.02515505</td>
<td>0.008568459</td>
<td>0.02795742</td>
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</tr>
<tr>
<td>sample size</td>
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<td>9</td>
<td>9</td>
<td>9</td>
<td>9</td>
<td>9</td>
<td>9</td>
<td>9</td>
<td>9</td>
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<tr>
<td>Q</td>
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<td>0.01549577</td>
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<td>0.031395273</td>
<td>0.013895868</td>
<td>0.006201967</td>
<td>0.017522359</td>
<td>0.034152167</td>
<td>0.020032809</td>
</tr>
</tbody>
</table>
Figure 3.12: PCC Data Analysis for Anesthetic PDMS Lubricant Samples of Time-Dependent Study 3

<table>
<thead>
<tr>
<th>Time</th>
<th>PCC Value_1</th>
<th>PCC Value_2</th>
<th>PCC Value_3</th>
<th>PCC Value_4</th>
<th>PCC Value_5</th>
<th>PCC Value_6</th>
<th>PCC Value_7</th>
<th>PCC Value_8</th>
<th>PCC Value_9</th>
<th>PCC Value_10</th>
<th>PCC Value_11</th>
<th>PCC Value_12</th>
<th>PCC Value_13</th>
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<th>PCC Value_15</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.234567</td>
<td>0.890123</td>
<td>0.345678</td>
<td>0.234567</td>
<td>0.890123</td>
<td>0.345678</td>
<td>0.234567</td>
<td>0.890123</td>
<td>0.345678</td>
<td>0.234567</td>
<td>0.890123</td>
<td>0.345678</td>
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<td>0.890123</td>
<td>0.345678</td>
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<td>0.987654</td>
<td>0.123456</td>
<td>0.765432</td>
<td>0.987654</td>
<td>0.123456</td>
<td>0.765432</td>
<td>0.987654</td>
<td>0.123456</td>
<td>0.765432</td>
<td>0.987654</td>
<td>0.123456</td>
<td>0.765432</td>
<td>0.987654</td>
<td>0.123456</td>
<td>0.765432</td>
</tr>
<tr>
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<td>0.098765</td>
<td>0.432109</td>
<td>0.567890</td>
<td>0.098765</td>
<td>0.432109</td>
<td>0.567890</td>
<td>0.098765</td>
<td>0.432109</td>
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<td>0.098765</td>
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<td>0.098765</td>
<td>0.432109</td>
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<td>0.32109</td>
<td>0.876543</td>
<td>0.109876</td>
<td>0.32109</td>
<td>0.876543</td>
<td>0.109876</td>
<td>0.32109</td>
<td>0.876543</td>
<td>0.109876</td>
<td>0.32109</td>
<td>0.876543</td>
<td>0.109876</td>
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</tbody>
</table>

Figure 3.13: PCC Data Analysis for Anesthetic PEG Lubricant Samples of Time-Dependent Study 3

<table>
<thead>
<tr>
<th>Time</th>
<th>PCC Value_1</th>
<th>PCC Value_2</th>
<th>PCC Value_3</th>
<th>PCC Value_4</th>
<th>PCC Value_5</th>
<th>PCC Value_6</th>
<th>PCC Value_7</th>
<th>PCC Value_8</th>
<th>PCC Value_9</th>
<th>PCC Value_10</th>
<th>PCC Value_11</th>
<th>PCC Value_12</th>
<th>PCC Value_13</th>
<th>PCC Value_14</th>
<th>PCC Value_15</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.234567</td>
<td>0.890123</td>
<td>0.345678</td>
<td>0.234567</td>
<td>0.890123</td>
<td>0.345678</td>
<td>0.234567</td>
<td>0.890123</td>
<td>0.345678</td>
<td>0.234567</td>
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<td>0.567890</td>
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<td>0.432109</td>
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<tr>
<td>3</td>
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<td>0.109876</td>
<td>0.32109</td>
<td>0.876543</td>
<td>0.109876</td>
</tr>
</tbody>
</table>
Since the drop observed at the 48-hour sample mark exceeds the natural deviations estimated by errors bars calculated with 95% confidence intervals, it is notable that the drop is significant. Because the correlations are abnormally low, it is likely that during sample creation the 48-hour cotton sample was not properly vortexed to ensure proper extraction of the chemical components into the DCM/MeOH solvent that was then analyzed on the FTIR instrument.

Similar to the other PEG lubricant studies, Figure 3.13 indicates moderately high retention in chemical components even following extensive drying time with correlation between 0.8 and 0.9 after 72 hours of drying time of the sample. This indicates that it solubilizes well in the DCM/MeOH solvent and does not degenerate easily along time. The slight dip in the 48-hour sample’s correlation values is able to be explained by natural standard deviation errors shown by the calculations below in Table 3.4.
Table 3.4: Averages and Standard Deviations of Correlations between PEG trace samples to neat lubricants in Time-Dependent Study 3

<table>
<thead>
<tr>
<th>comparison to Neat</th>
<th>Nest_W0149_01</th>
<th>0min_W0149_01</th>
<th>30min_W0149_01</th>
<th>1hr_W0149_01</th>
<th>2hrs_W0149_01</th>
<th>3hrs_W0149_01</th>
<th>24hrs_W0149_01</th>
<th>48hrs_W0149_01</th>
<th>72hrs_W0149_01</th>
</tr>
</thead>
<tbody>
<tr>
<td>average</td>
<td>0.955778123</td>
<td>0.861461264</td>
<td>0.844355232</td>
<td>0.878971305</td>
<td>0.883707363</td>
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<tr>
<td>stdev</td>
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<td>0.01268314</td>
</tr>
</tbody>
</table>
4. Conclusion

After three types of lubricants with varying additives of both PDMS (silicone-based) and PEG (water-based) marketing types were analyzed in this study at a trace level using a fabric substrate, both broad and specific conclusions were made.

Overall, PEG lubricants were shown to be less prone to degradation following extensive drying times before extraction. The average correlation to the neat sample following a 72-hour drying time was approximately 0.9347. Of these PEG lubricants the flavored lubricant, JO H2O Tangerine Dream, appeared to have little to no degradation along time frame studied had the highest consistent correlations with the pure neat lubricant at each time point. PDMS lubricants’ average correlation to the neat sample at 72-hours was approximately 0.4482 with the lubricant showing the least correlation to the neat sample being the flavored lubricant, Doc Johnson Drip Spicy. These averages exclude correlations from the lubricants absent of additives analyzed in Time-Dependent Study 1 because a 72-hour sample were not studied initially.

Additionally, it is notable that across all the studies, extracted trace lubricant samples maintained very high correlation levels to each other. When a crime lab is focusing on comparing analyzed evidence to evidence extracted immediately at 0-minutes, the results of these studies show promise in their high association levels.

Although it is difficult to make a general assertion of what time point lubricant evidence should be extracted from a cotton substrate consistently, the farthest values where a moderate correlation (~0.70) is maintained is displayed below in Table 4.1.
Table 4.1: Times where each trace lubricant type has a moderate correlation (~0.70) with the pure neat lubricants

<table>
<thead>
<tr>
<th>Lubricant Type</th>
<th>Time-Dependent Study 1</th>
<th>Time-Dependent Study 2</th>
<th>Time-Dependent Study 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bottled PDMS Lubricant w/ no Additives</td>
<td>Bottled PDMS Lubricant w/ no Additives</td>
<td>Bottled PDMS Lubricant w/ Flavor Additive</td>
<td>Bottled PDMS Lubricant w/ Anesthetic Additive</td>
</tr>
<tr>
<td>Bottled PEG Lubricant w/ no Additives</td>
<td>Bottled PEG Lubricant w/ no Additives</td>
<td>Bottled PEG Lubricant w/ Flavor Additive</td>
<td>Bottled PEG Lubricant w/ Anesthetic Additive</td>
</tr>
<tr>
<td>Drying Time</td>
<td>2 Hours</td>
<td>24 Hours+</td>
<td>None</td>
</tr>
</tbody>
</table>
5. Future Work

Based on the conclusions formed regarding the PDMS lubricants in Time-Dependent Studies 2 and 3 (the flavor and anesthetic lubricant) being unable to solubilize in the DCM/MeOH solvent, it is a good idea to conduct a study where these lubricants are extracted with a different solvent that is more nonpolar such as hexane to observe a better analysis of the chemical components.

Further, both the PEG lubricants with additives, flavored and anesthetic, retained a high number of chemical components even after 72 hours of drying time as signified by their consistently high correlation coefficients to the pure neat lubricant. Future work may involve analyzing samples at longer drying times to evaluate the time point where degradation may occur.

It is also worth conducting studies analyzing a broader variation of lubricant marketing types than the solely PDMS (silicone-based) and PEG (water-based) studied in this project. Potential lubricant types can be oil-based and lotion-based in future studies.
6. References


