The detection and discrimination of sunless self-tanners containing dihydroxyacetone on clothing using instrumental techniques

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THE DETECTION AND DISCRIMINATION OF SUNLESS SELF-TANNERS CONTAINING DIHYDROXYACETONE ON CLOTHING USING INSTRUMENTAL TECHNIQUES

by

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ABSTRACT

The awareness of health risks associated with sun exposure, primarily ultraviolet (UV) radiation, have played a large role in the introduction of sunless self-tanning products. These products, produced by cosmetic companies, are intended to provide the user with a sun-tanned appearance without exposing the skin to harmful UV radiation. While the manufacturers of these products claim that the products are transfer-free, several reports of the tanner depositing onto the wearers clothing have been documented. As this is a highly undesirable characteristic for the consumer, the product’s ability to transfer onto clothing makes sunless self-tanners a potentially valuable piece of forensic evidence in cases where an altercation between two individuals has occurred, specifically in sexual assaults, beatings, and homicides. The presence of self-tanner on an individual’s clothing could help corroborate a story and provide an additional piece of evidence and/or leads to an investigation.
The purpose of this study was to determine if sunless self-tanners transfer from skin to clothing. Given that a transfer occurs, this research was also intended to both identify and evaluate the differences seen between self-tanning products using instrumental techniques that would typically be used in forensic labs.

Sixteen sunless self-tanning products were added to the skin as directed by the manufacturer. After an assigned time interval since application (15 minutes, 30 minutes, 1 hour, 3 hours, 6 hours, or 12 hours) was reached, a white cotton swatch was used to wipe a portion of the sunless self-tanner off of the skin in attempt to simulate a realistic scenario of an altercation between individuals who may be wearing the product. Observations of the cotton swatches were documented. Transferred material on the cotton swatches was analyzed using Fourier Transform Infrared Spectroscopy (FTIR). Analysis of the products prepared directly from the packaging as well as two samples containing transferred material were analyzed using Gas Chromatography- Mass Spectrometry (GC-MS).

All of the sixteen samples transferred from the skin onto the cotton swatch when forcibly wiped at each time interval. FTIR analysis was unable to discriminate between the commercial products but was able to separate the samples into six groups based on similarities seen between the spectra. Analysis using this instrumental technique was useful in identifying the samples as sunless self-tanning products, but was unable to differentiate further. Analysis of the sunless self-tanners prepared directly from their packaging/bottle using GC-MS
was able to differentiate between the products, providing a combination of chemical ingredients that were unique to each product. Analysis of the transferred material on the cotton swatches did not identify all of the chemical components that were earlier considered unique to that sample, however, peaks were observed in the chromatogram that were also present in the samples when prepared directly from their packaging. These transferred samples were able to be identified when a known sample was available for comparison. The instrumental techniques used in this study are useful in analyzing and identifying suspected sunless self-tanner stains on clothing in a crime laboratory setting. The results obtained from this analysis can provide probative information in an investigation.
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LIST OF ABBREVIATIONS

ALS.................................................................Alternate Light Source
ATR............................................................Attenuated Total Reflectance
DMI.............................................................Dimethylisosorbide
DHA..............................................................Dihydroxyacetone
EU...............................................................European Union
FDA.............................................................Food and Drug Administration
FTIR............................................................Fourier Transform Infrared Spectroscopy
GC...............................................................Gas Chromatography
GC-MS.........................................................Gas Chromatography-Mass Spectrometry
HPLC.............................................................High Performance Liquid Chromatography
IR...............................................................Infrared
MS..............................................................Mass Spectrometry
SC..............................................................Stratum Corneum
SPF.............................................................Sun Protective Factors
UV...............................................................Ultra Violet
1. INTRODUCTION

1.1 BACKGROUND

Health risks associated with sun exposure, primarily ultra violet (UV) radiation, are well understood, however, a tanned complexion is still very popular in today's culture. Raised concerns by health organizations such as the American Cancer Society have prompted cosmetic companies to introduce an alternative to UV exposure, resulting in the production of sunless self-tanners that could be purchased over the counter at any drug store. These products are able to mimic the appearance of sun-tanned skin without exposing the skin to harmful UV rays, as the sun or a tanning bed would do. Sunless self-tanners were first commercially introduced approximately 60 years ago, primarily as a way to sustain a tanned complexion in the winter months. At that time, the sunless self-tanners had a fairly poor reputation as they were known to leave the skin an unnatural orange color that typically dried unevenly. Furthermore, the products were notorious for transferring onto the wearer's clothing. As the health risks associated with UV exposure became more apparent, cosmetic companies began to evolve their sunless tanners into a more reliable product that produced a more even tan and overall more natural appearance. While the manufactures claim that today's products are transfer-free, deposition of the tanners onto the wearer's clothing has still been noted, especially in areas of frequent contact and rubbing such as collars of shirts, sleeve cuffs, and waistbands.
Given that these products have the potential to transfer from skin to clothing, sunless self-tanners could provide useful evidentiary information in a forensic case where an altercation between individuals has occurred, primarily in sexual assaults, beatings, and homicides. If present, sunless self-tanners could transfer from a victim to a suspect, or vice versa, providing evidence that could then be analyzed within a crime laboratory and possibly provide valuable information in an investigation.

The purpose of this research was twofold; first, to determine whether sunless self-tanners transferred onto clothing could be detected and second, to determine whether different commercial products could be differentiated from one another using instrumental techniques. The methods utilized in this research can also serve as a protocol for others to analyze this type of evidence in the future.

1.2 SUNLESS SELF-TANNERS

The Food and Drug Administration (FDA) describes sunless self-tanners as a cosmetic intended to produce a tanned color change to the skin without the requirement of UV exposure\(^5\). Sunless self-tanners are available in several different application forms including lotions, aerosol sprays, foams, and saturated towelettes. The physical characteristics of each application form can differ in appearance and composition, especially among the lotions and foams. Products vary in color from white, to light brown, to dark brown. Many of the sunless self-tanners that are labeled as “instant action” are typically brown or darker in color, while others labeled “gradual tanners” tend to be lighter in color. It has been noted
in past studies that the majority of “instant” self-tanners have an additional bronzing component within them which is responsible for the initial color change seen, providing an “instant” tan. Apart from the color of the product, the presence of lustrous mica particles may also be present. The variation in the appearance of the products is dependent on the overall look desired by the consumer. Sunless self-tanners are available for purchase at most drug stores, online, and in tanning salons.

1.3 DISTRIBUTION OF USE OF SUNLESS SELF-TANNERS

The proportion of the population using sunless tanners varies between age groups, races, gender, and geographical area. Brooks et al. (2006) stated that of the 448 American participants in a survey on sunless tanning use, 95 (22%) claimed to use sunless self-tanners on a regular basis and an additional 98 (22%) stated that they considered future use of sunless self-tanners as an alternative to traditional tanning methods. Participants who stated that they use self-tanners were asked additional questions on their history of sun exposure and the reason for self-tanner use. The study found that the majority of the 193 participants who either used sunless tanners regularly or intended to use them in the future, were female and claimed to burn easily in the sun. 51% of the participants preferred sunless tanners because they are a safer alternative to sun exposure, 40% used them to obtain a tanned look for special events, 36% used them to maintain a tan in the winter months, and 29% stated that sunless tanning took less time than sitting in the sun. There may be other motives for the use of sunless self-tanners
by these participants, however, each of these options were provided by the surveyors, rather than open response answers from the participants.

Another study on sunless self-tanners in Australia produced similar results. Of the 1,509 participants, approximately 65% stated that tanned skin was more attractive than pale skin. An overwhelming majority (93%) of sunless tanner users in the study were female and above the age of 25 (85%). Similar to the American study, more self-tanner users than non-users claimed to burn in the sun and required the use of sunscreen during the summer months. Unlike the American study, the majority of the Australian participants claimed to use the sunless tanning products in the summer months only; however participants claimed to also use the products before special events, regardless of the time of year. When asked about the psychological effects of sunless self-tanners 61% of the participants in this study stated that they believed that the Cancer Council would be sending the wrong message to the public by promoting the use of sunless self-tanners, fearing that more people would assume that the product provides protection against UV radiation which would incidentally promote an increase in sun exposure.

Both of these studies, as well as others, have shown that individuals who have a fair complexion are more likely to use sunless self-tanners. These individuals are also at the highest risk of permanent skin damage. Melanoma is twenty times more likely among whites than African Americans and ten times more likely than everyone else. Melanoma is also the most common cancer among young adults in America. It is important for sunless self-tanner users, especially
those with a lighter skin complexion to understand that while the self-tanners give the appearance of a sun tanned look, these products do not provide protection from the sun. Past studies have revealed that at the time of application, components of sunless tanners provide an SPF (sun protective factor) of 3 for approximately 24 hours\(^4\). While self-tanners provide slight UV protection, it is temporary and is not a substitute for sunscreen.

### 1.4 THE CHEMISTRY OF SUNLESS SELF-TANNERS

Sunless self-tanners vary in color and application type, however, the active ingredient which produces the color change remains consistent between each product. Dihydroxyacetone (DHA) is a colorless dye that when added to the skin, reacts with free amino acids in stratum corneum (SC)\(^8\), the outermost layer of the skin, creating a semi-permanent brown color change\(^7,8\). Studies have shown that DHA reacts most readily with lysine, glycine, and histidine, which are all present in the stratum corneum\(^8\). This reaction is known as the Maillard reaction which was first used to describe the browning of meats as they cooked\(^1\).

DHA (C\(_3\)H\(_6\)O\(_3\)) is a small polar carbohydrate found in sugar cane, as well as an intermediate in the metabolism of more complex carbohydrates in higher plants and animals\(^1\). DHA can be in the form of either a monomeric solid as a white, crystalline, hygroscopic powder, or in aqueous solutions, where it is typically found as a dimer.
DHA was introduced as a possible medical substitute for glucose in diabetic patients in the 1950's\textsuperscript{3,7,9}. The color changing properties of DHA were first discovered at the University of Cincinnati Children’s Hospital where doctors conducted a DHA tolerance test for glycogen storage disease\textsuperscript{7}. Patients were given the medication orally in increasing doses until the patient subsequently threw up. A brown color change developed on the patient's skin where the regurgitated medication had landed\textsuperscript{7,9}. This unexpected observation resulted in further experimentation with DHA, eventually leading to its present day purpose as a colorant in sunless self-tanners.

Since these early studies, cosmetic companies have developed a wide variety of sunless self-tanning products. Differences seen between products include the application type, the intensity of the tan produced, the presence of sparkling mica pigments, and the number of application needed for a tan to become visible on the skin\textsuperscript{3,10}. Some sunless self-tanning products are labeled as “gradual tanners” or “gradual moisturizers” whereas other sunless self-tanners require only one application for a tan to become visible. Sunless self-tanners that are intended to be used gradually have lower levels of DHA and are applied as a daily moisturizer. With each application the intensity of the tan increases\textsuperscript{11}. 

\begin{figure}
\centering
\includegraphics[width=\textwidth]{images/diagram.png}
\caption{Chemical Structure of dihydroxyacetone monomer (left) and dimer (right)}
\end{figure}
Sunless self-tanners that require only one application contain slightly higher levels of DHA and produce an artificial tan within 2-3 hours after application as the DHA reacts with the amino acids in the stratum corneum (SC) layer of the skin\(^9,11\). Some of these products are labeled as “instant action tanners” and frequently contain an additional bronzing agent that temporarily dyes the skin on contact while the DHA reacts with the amino acids\(^9\). These added bronzing agents are temporary dyes which wash off upon bathing. They are used as a temporary and immediate color replacement for the longer lasting tan produced by the DHA\(^9\).

DHA is the most commonly used colorant in sunless tanners, however, there are some drawbacks associated with the ingredient. DHA is known to become unstable over time\(^12-16\) which can affect both the shelf-life and the overall appearance of the product when used. Other products within the sunless self-tanners may react with the DHA, reducing the stability and shelf-life of the product. As DHA becomes less stable, a foul smell has been reported\(^12\). It has been speculated that the large quantity of fragrance ingredients found in sunless self-tanners have two purposes: (1) to provide a pleasant smell, and (2) to mask the smell of the unstable DHA when it has started to react with other ingredients in the product\(^12\). Efforts have been made to improve the stability of DHA, including lowering the pH to a more acidic solution, however, by doing so, the product is more likely to cause irritation to the skin\(^13\). Other colorants such as sodium coco-sulfate\(^16\), caramel\(^17\), and canthaxanthin\(^18\) have also been introduced to replace DHA as the active ingredient in sunless tanners. These substitutes have proven
to be more stable, but the tan produced has been described to be less attractive than tans produced by DHA containing products. Furthermore, canthaxanthin has been linked to harmful side effects and has been banned in some countries\textsuperscript{18,19}.

1.5 SUNLESS SELF-TANNERS AS FORENSIC EVIDENCE

Cosmetic companies have improved their products, yet there are still several reports today of the products transferring onto the wearer’s clothing\textsuperscript{3,12,13,20}. This characteristic may be undesirable for the consumer, however, it could potentially be very useful in a forensic setting. In a scenario in which a physical altercation happens between two individuals, there is a possibility that self-tanners could be transferred from one individual’s skin onto the other’s clothing. The transfer of material from one object to another is based on a theory known as Locard’s principle of exchange. Locard’s principle states that every contact leaves a trace, meaning that if two items come in contact with one another, it is possible that each item will leave behind a portion of itself on the other object. Whether there is an exchange of material between items is dependent on several factors, as the nature of the two items affects their ability to transfer. Factors affecting the ability to transfer include the length of time the two items have been in contact with one another, the overall area/size of the contact site, the force that was applied to the two items while in contact, environmental factors before, during, and after the contact, and whether either item was altered in any way after the contact. In the case of sunless self-tanners, the factors that could presumably affect its transfer from skin onto clothing include the amount of time since the tanner was applied,
the force applied to the skin, the area of the body in which the tanner was located, the number of times the product has been applied to the skin, the brand of tanner, and the application form of the product, whether it be a lotion, spray, foam, or towelette.

Assuming that sunless self-tanners could be transferred onto clothing, and subsequently collected as forensic evidence in an investigation, the detection and identification of the self-tanner would become the responsibility of analysts in the trace evidence section of the crime laboratory. Analysis of the stain would presumably follow a similar protocol to the examination of miscellaneous or cosmetic evidence. The analytical procedure of cosmetics starts with a visual description of the stain under white light, and a stereomicroscope, followed by examination under a polarized light microscope to determine the pigment, size of particles, birefringence, presence of mica flakes, and extinction of the particles. Analysis under a polarized light microscope is the most useful when you have a known sample to which the item of evidence could be compared to. Unknown cosmetic samples are also analyzed instrumentally using Fourier Transform Infrared Spectroscopy (FTIR) and Gas Chromatography-Mass Spectrometry (GC-MS). This type of analysis does not require a known sample for comparison and can compare the sample results to chemical libraries, potentially identifying the unknown sample.
1.6 INSTRUMENTATION

1.6.1. FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

Each molecule is unique in that the chemical makeup and formation of the bonds act in characteristic ways when exposed to an energy source. The Fourier Transform Infrared Spectrometer (FTIR) introduces an infrared light source to the sample causing the vibration and rotation of the bonds of the molecules. The energy differences, due to the vibration and rotation of the molecular bonds, are absorbed and detected by the instrument producing a spectral readout of the frequencies of each vibration and rotation. The spectra produced for any given sample is highly reproducible. This reliability and reproducibility allows for the comparison and identification of unknown items through the use of a spectral library search.

FTIR is a non-destructive instrumental technique and allows for the analysis of solid, liquid, and vapor samples. There are several different attachments available that allow for the analysis of different sample types. One of which is a horizontal-attenuated total reflectance (horizontal-ATR) attachment. The horizontal-ATR is a sample chamber containing an infrared-transparent prism that directs the infrared (IR) beam to the sample area. The prism produces several internal reflections causing the IR beam to penetrate only a small distance into the sample. This requires that the sample be in intimate contact with the prism in order to obtain a sufficient absorption spectrum.
Another attachment used in conjunction with the FTIR is a microscope which utilizes aluminum coated surfaces for reflection purposes unlike a compound microscope which uses glass mirrors for reflection of the IR beam. The microscope is typically used in transmission mode, in which the light of the microscope passes through the sample from bottom to top rather than reflecting off of the sample area.

A diamond anvil/compression cell can be used in conjunction with the microscope attachment of the FTIR. The diamond compression cell is a sampling vessel that may be used when there is little sample available for analysis. It is comprised of two diamond windows that compress and thin the sample allowing the transmitted light source to easily pass through the sample area to obtain an IR spectrum.

1.6.2 GAS CHROMATOGRAPHY/ MASS SPECTROMETRY (GC-MS)

Chromatography is an analytical method of separating molecules based on their affinity for either the mobile phase or the stationary phase. In gas chromatography (GC), the stationary phase is typically a fused silica column with either a helium or hydrogen carrier gas (mobile phase). The sample is injected onto the column as a gas where it interacts with the stationary phase (the column). Using this analytical technique, mixtures can be separated into individual
components. The separation of molecules is dependent on each component’s size, polarity, and affinity for the stationary phase. Small molecules typically interact with the column less and tend to elute off of the column faster than larger molecules.

Coupled to the GC is the mass spectrometer (MS) which detects and analyzes each of the individual components of a given sample based on their mass-to-charge ratio as they are eluted from the column of the GC. The data from the MS is collected and interpreted using computer software, producing a chromatogram which displays the retention time and the abundance of each component detected. Peaks displayed in the chromatogram can be compared to known chemicals in an internal library for identification. Like the FTIR, GC-MS analysis provides reliable and reproducible results making it a useful tool when analyzing unknown substances.
2. MATERIALS

All of the sunless self-tanner samples (see Error! Reference source not found.) used were purchased at either drugstores or cosmetic supply stores. The 4 inch by 4 inch Cotton Wipers (TX304) were purchased from TexWipes (Kernersville, NC). Number 10 and 11 disposable Surgical Scalpel Blades were purchased from Miltex Carbon Steel (York, PA). The following chemicals were purchased from Thermo Fisher Scientific (Waltham, MA): Acetone (Optima™), Acetone (HPLC), Ethyl Acetate (HPLC), Methanol (Laboratory), and Glycerin. The dihydroxyacetone standard was purchased from U.S. Pharmacopeial Convention (Rockville, MD). The caramel coloring was purchased from Spectrum Chemical Manufacturing Corp via Fisher Scientific (Pittsburgh, PA). Sterile Cotton Tipped Applicators were purchased from Puritan (Guilford, ME). Pipettes used were purchased from Rainin through Mettler Toledo (Columbus, OH). ST-IR Polyethylene cards (model 0020-300) were purchased from Thermo Scientific Nicolet (Waltham, MA). The model of the Fourier Transform Infrared Spectrometer used was Thermo (Waltham, MA) with a Nicolet6700 horizontal-Attenuated Total Reflectance attachment, Nicolet Continuum microscope attachment, and a Microsample Diamond Compression Cell Kit with two mounted diamond windows and insertion tool 0045-344. All IR spectra were analyzed using OMNIC 7.3 software. The model of the Gas Chromatograph system used was Agilent Technologies 6890 Series with a 7683 Series Injector (Santa Clara, CA) and an Agilent Technologies J&W DB-225MS column (length: 30 meters, diameter: 0.250
mm, film: 0.25 µm, 40°C-240°C). The model of the Mass Spectrometer used was Agilent Technologies 5973 Network Detector. All chromatograms were analyzed using Agilent MSD Enhanced ChemStation D.03.00.611. All chemical structures were created using Marvin Sketch version 6.2.2. made by ChemAxon Ltd of Cambridge, MA.

Table 1. List of samples used in the study. All samples were purchased at either a drug store or cosmetic store.

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Brand</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Olay</td>
<td>Quench Plus Touch of Sun Body Lotion</td>
</tr>
<tr>
<td>2</td>
<td>L'Oreal Paris</td>
<td>Sublime Bronze Luminous Bronzer Self-Tanning Lotion</td>
</tr>
<tr>
<td>3</td>
<td>L'Oreal Paris</td>
<td>Sublime Bronze Natural Tinted Self-Tanning Lotion</td>
</tr>
<tr>
<td>4</td>
<td>Coppertone</td>
<td>Endless Summer, Gradual Tanning Lotion</td>
</tr>
<tr>
<td>5</td>
<td>CVS</td>
<td>Sunless Tinted Lotion</td>
</tr>
<tr>
<td>6</td>
<td>Jergen’s</td>
<td>Natural Glow Revitalizing Daily Moisturizer</td>
</tr>
<tr>
<td>7</td>
<td>Banana Boat</td>
<td>Summer Color Self-Tanning Lotion</td>
</tr>
<tr>
<td>8</td>
<td>Neutrogena</td>
<td>Build-a-Tan Gradual Sunless Tanning Lotion</td>
</tr>
<tr>
<td>9</td>
<td>Equate</td>
<td>Beauty Flawless Self-Tan Bronzing Mist</td>
</tr>
<tr>
<td>10</td>
<td>L’Oreal</td>
<td>Sublime Bronze ProPerfect Salon Airbrush Self-Tanning Mist</td>
</tr>
<tr>
<td>11</td>
<td>Neutrogena</td>
<td>Micro Mist Airbrush Sunless Tan</td>
</tr>
<tr>
<td>12</td>
<td>Banana Boat</td>
<td>Summer Color Self-Tanning Mist</td>
</tr>
<tr>
<td>13</td>
<td>Jergen’s</td>
<td>Natural Glow Lightweight Foaming Daily Moisturizer</td>
</tr>
<tr>
<td>14</td>
<td>L'Oreal</td>
<td>Sublime Bronze Self-Tanning Towelettes</td>
</tr>
<tr>
<td>15</td>
<td>St. Tropez</td>
<td>One Night Only: Instant Glow Body Lotion</td>
</tr>
<tr>
<td>16</td>
<td>Viva Liberata</td>
<td>Tinted Self Tan Mousse for Body</td>
</tr>
</tbody>
</table>
3. METHODS

3.1. CLASSIFICATION OF SAMPLES

The sixteen self-tanning samples used in the study were purchased from drug, convenience, or cosmetic stores. Each of the samples were categorized based on their application type: lotion, foam/mousse, spray, or towelette. The color and general appearance of each sample was documented. It was also noted whether the samples were intended for one time application or to be used as a daily moisturizer.

3.2. SOLUBILITY OF SUNLESS SELF-TANNERS

Each of the samples were added to 1000µl of the three solvents tested: methanol, acetone, and ethyl acetate. For the lotion and foam samples, a drop of the sample was added to a cotton swab which was then immediately placed into the solvent. The liquid spray samples were sprayed directly into the vial for approximately half of a second, followed by the addition of the solvent. For the towelette, a disposable pipette was used to extract the liquid in the bottom of the towelette’s packaging. One drop of the extracted liquid was added to the solvent vial. Each of the samples were agitated for approximately 5 minutes and the solubility of each was recorded to determine the extraction solvent best suited for each sample.
3.3. PREPARATION OF REFERENCE SAMPLES

Observations of the appearance of each sample added directly onto a cotton swatch from the product packaging was recorded and photographed to use as a reference for the transfer study. Each of samples were also visualized using an alternate light source at 455nm and 535nm.

A reference IR-spectrum of each sample was created using two different methods. The first method utilized polyethylene cards. Each of the samples were added to a polyethylene card and allowed to dry overnight. The samples were then analyzed using the FTIR bench top. The second method utilized the FTIR with a horizontal-ATR attachment and a DuraSampIR volatiles cap sampling vessel. A drop of each of the samples was added to the sampling area of the horizontal-ATR and covered with the DuraSampIR volatiles cap. Three spectra were created of each sample and used as a comparison for all of the future samples analyzed in the study.

3.4. TRANSFER STUDY

3.4.1. APPLICATION OF THE SUNLESS SELF-TANNING SAMPLES

Each of the samples were applied as directed by the manufacturer to the skin in a rectangular pattern. The location of application for each sample differed based on available space, but were limited to the arms, upper legs, and stomach. To avoid mixing samples, the sunless self-tanners were spaced at least one inch away from each other on the skin and were applied with gloves that were changed between each application. Samples that were intended to be used as a gradual
tanning daily moisturizer (samples 1, 4, 6, 7, 8, and 13) were applied to the skin in two separate areas, one area to be tested on the day of the first application, labeled “1X” and one area to be tested after three days of application, labeled “3X”. No other cosmetic products or lotions were added to the skin over the course of the study. General observations, including the time at which a color change was apparent, drying time, the evenness of the tan, and the length of time the tan lasted were recorded for each sample.

To assess whether the sunless self-tanners transfer in a time dependent manner since their application, the tanned area of the skin was separated into six evenly sized sections, each of which were assigned with a “time since application” label: 15 minutes, 30 minutes, 1 hour, 3 hours, 6 hours, or 12 hours. These designated time intervals were separated from one another by drawing a line with a pen or fine tipped permanent marker to create evenly sized sections that were approximately 1.5 inches by 1.5 inches, similar to what can be seen in Figure 3.

<table>
<thead>
<tr>
<th>15 min</th>
<th>30 min</th>
<th>1 hr</th>
<th>3 hr</th>
<th>6 hr</th>
<th>12 hr</th>
</tr>
</thead>
</table>

*Figure 3. General outlay of the sample area on the skin and the assigned time intervals*

Once the samples were evenly applied, a timer was started and when the allotted time was reached for a given section, a white 4 inch by 4 inch cotton swatch was used to attempt to wipe off the sunless self-tanner in that area. Assuming that an altercation between two individuals would be violent, a substantial amount of force was used in an attempt to wipe the self-tanner off of the skin. Any color
changes to the cotton, both immediately after wiping and those that developed at a later time, were documented. Photographs were taken of all of the cotton swatches. Any alterations to the skin, apart from redness, were also noted.

Over the course of this study, normal daily activities were carried out, including exercising and bathing. The clothes worn during the testing period were typical of a normal day’s outfit and no attempts were made to purposely avoid or agitate the tanned area with the clothing. While the tanners were being purposely transferred onto the designated cotton swatches, any unintended transfer onto the wearer’s clothing was noted, but not analyzed.

3.4.2. ANALYSIS OF COTTON SWATCHES

3.4.2.1 METHOD DEVELOPMENT FOR EXTRACTION OF SAMPLES

Three methods were evaluated to determine the best method for extracting the transferred self-tanners off of the cotton swatches for further analysis. The first method utilized cotton swabs dampened with acetone. Two swabs were rolled over the stained area to pick up traces of the sunless self-tanners. Half of one swab was placed in a vial with 500 µl of acetone and allowed to extract on a sample rocker for a minimum of three hours. The samples were then placed in a porcelain well plate to allow the acetone to evaporate, leaving the extracted sample behind.

The second method tested used a cutting of the stained cotton swatch approximately 0.5 cm by 0.5 cm in size. The cutting was placed in a vial with 500 µl of acetone and allowed to extract on a sample rocker for a minimum of three hours. The samples were placed in a well plate to allow the acetone to evaporate,
leaving the extracted samples behind. For both of these methods, the extractions were analyzed using a horizontal-ATR attachment with a DuraSamplIR volatiles cover. Samples were placed on the sample area along with one drop of acetone and covered with the DuraSamplIR cover. Pure acetone was used as the background.

The third method utilized to extract the sunless self-tanners from the cotton swatches was a scraping method. Under a stereomicroscope, a scalpel blade was used to scrape the surface of the stained area of the cotton. The scrapings were added directly to a diamond compression cell and analyzed using the microscope attachment of the FTIR.

For all three of these methods, the positive controls used were the samples added directly to the cotton swatches and the spectra created from the commercial samples prepared directly from the packaging. The negative control was a cotton swatch that wiped unaltered, non-tanned skin.

3.4.2.3. FTIR PARAMETERS

Samples extracted from the cotton swatch were analyzed using Fourier Transform Infrared Spectroscopy (FTIR). To visualize the spectra that each sample would presumably produce, a drop of each sunless self-tanner was added directly to polyethylene IR sample cards, allowed to dry, and analyzed using the horizontal ATR attachment of the FTIR in triplicate. Inconsistent spectra lead to a second method of FTIR analysis. Sunless self-tanners were added directly from
the bottle to the sample area of the FTIR bench top and covered with a DuraSampIR volatiles cap. Three spectra were collected for each sample.

All of the transferred material of samples that were present on the cotton swatches were scraped off of the cotton using a scalpel blade and added to the sample area of a diamond compression cell and analyzed using the microscope attachment of the FTIR. Three spectra were collected for each transferred sample. Spectra of cotton swatches that had wiped unaltered skin were used as a negative control and subtracted from each of the sample spectra using OMNIC software. These spectra were then compared to the known spectra of the samples obtained earlier.

3.4.2.4. GC-MS PARAMETERS

GC-MS analysis was performed on sunless self-tanner samples taken directly from their bottles. A dilution series containing 0.25%, 0.1%, 0.05%, 0.03%, and 0.01% DHA was created for the four liquid spray samples (9, 10, 11, 12). For this dilution series, it was assumed, based on previous research, that the DHA content of each product was 5%. Each of the samples in the series were analyzed using GC-MS to determine the amount of DHA needed to detect the chemical components in each sample without overloading the column. The most optimal sample percentage was used for the preparation of the remaining 12 samples.

The original method used for GC-MS analysis was based on parameters set by Lili et al. (2006) in their analysis of dihydroxyacetone and glycerol in fermentation broth and then modified to optimize peak resolution and run time.
For each of the methods acetone was used as the solvent, the injection volume was 2 µl and remained split-less, and the helium carrier gas was at a constant flow. The GC column used was atypical in that it was a polar column. This allowed for the small polar components of the tanner, such as DHA, to have a higher affinity for the column rather than eluting off of the column with the solvent and go undetected as they may have with a typical non-polar column. The parameters set for each of the methods were as follows:
### Table 2. GC-MS Parameters

<table>
<thead>
<tr>
<th>Method</th>
<th>Temp</th>
<th>Pressure (psi)</th>
<th>Total Flow</th>
<th>Purge Flow</th>
<th>Gas Saver</th>
<th>Initial Temp</th>
<th>Hold</th>
<th>Ramp 1</th>
<th>Temp</th>
<th>Hold</th>
<th>Ramp 2</th>
<th>Final Temp</th>
<th>Hold</th>
</tr>
</thead>
<tbody>
<tr>
<td>DHA1</td>
<td>250°C</td>
<td>7.63</td>
<td>30</td>
<td>25.5 mL/min</td>
<td>20 mL/min @ 2 min</td>
<td>50°C</td>
<td>0</td>
<td>1°C/min</td>
<td>60°C</td>
<td>0</td>
<td>10°C/min</td>
<td>280°C</td>
<td>0</td>
</tr>
<tr>
<td>DHA2</td>
<td>30°C</td>
<td>4.22</td>
<td>12.4</td>
<td>8.0 mL/min</td>
<td>20 mL/min @ 2 min</td>
<td>30°C</td>
<td>1 min</td>
<td>3°C/min</td>
<td>50°C</td>
<td>0</td>
<td>-</td>
<td>50°C</td>
<td>0</td>
</tr>
<tr>
<td>DHA3</td>
<td>20°C</td>
<td>4.21</td>
<td>12.4</td>
<td>8.0 mL/min</td>
<td>20 mL/min @ 2 min</td>
<td>30°C</td>
<td>1 min</td>
<td>3°C/min</td>
<td>50°C</td>
<td>0</td>
<td>20°C/min</td>
<td>250°C</td>
<td>0</td>
</tr>
<tr>
<td>DHA4</td>
<td>20°C</td>
<td>4.21</td>
<td>12.4</td>
<td>8.0 mL/min</td>
<td>20 mL/min @ 2 min</td>
<td>30°C</td>
<td>1 min</td>
<td>3°C/min</td>
<td>50°C</td>
<td>0</td>
<td>20°C/min</td>
<td>250°C</td>
<td>0</td>
</tr>
<tr>
<td>DHA5</td>
<td>50°C</td>
<td>5.25</td>
<td>12.4</td>
<td>8.0 mL/min</td>
<td>20 mL/min @ 2 min</td>
<td>50°C</td>
<td>0</td>
<td>25°C/min</td>
<td>250°C</td>
<td>0</td>
<td>-</td>
<td>250°C</td>
<td>0</td>
</tr>
<tr>
<td>DHA6</td>
<td>50°C</td>
<td>5.25</td>
<td>12.4</td>
<td>8.0 mL/min</td>
<td>20 mL/min @ 2 min</td>
<td>50°C</td>
<td>0</td>
<td>25°C/min</td>
<td>250°C</td>
<td>0</td>
<td>10°C/min</td>
<td>280°C</td>
<td>3 min</td>
</tr>
</tbody>
</table>

### MS Parameters

<table>
<thead>
<tr>
<th>Method</th>
<th>Tune File</th>
<th>Scan Mode</th>
<th>Solvent Delay</th>
<th>Mass Range (amu)</th>
<th>Total Scan Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>DHA1</td>
<td>atune.u</td>
<td>Scan Mode</td>
<td>3.0 min</td>
<td>50-500</td>
<td>32 min</td>
</tr>
<tr>
<td>DHA2</td>
<td>atune.u</td>
<td>Scan Mode</td>
<td>0 min</td>
<td>30-500</td>
<td>7.67 min</td>
</tr>
<tr>
<td>DHA3</td>
<td>atune.u</td>
<td>Scan Mode</td>
<td>0 min</td>
<td>30-500</td>
<td>17.67 min</td>
</tr>
<tr>
<td>DHA4</td>
<td>atune.u</td>
<td>Scan Mode</td>
<td>4.5 min</td>
<td>30-500</td>
<td>17.67 min</td>
</tr>
<tr>
<td>DHA5</td>
<td>atune.u</td>
<td>Scan Mode</td>
<td>4.5 min</td>
<td>30-500</td>
<td>8 min</td>
</tr>
<tr>
<td>DHA6</td>
<td>atune.u</td>
<td>Scan Mode</td>
<td>4.5 min</td>
<td>30-500</td>
<td>14 min</td>
</tr>
</tbody>
</table>

* DHA1: Parameters set by Lili et al
* DHA2: Isothermal with shallow temperature gradient
* DHA3: Decreased injection port temperature to avoid thermal degradation
* DHA4: Solvent delay to remove acetone carry over from the blank
* DHA5: Shortened run time by editing the temperature gradient
* DHA6: Extended run by 3 minutes after temperature gradient
For the analysis of the transferred material on the cotton swatches, two samples, sample 7(3X) and sample 9, were chosen for analysis based on the relative amount of material present on the cotton swatch and the distribution of peaks seen in the chromatograms of these commercial products. Cuttings measuring approximately 1 cm x 1 cm were taken from the following three time intervals for each of the samples: Sample 7(3X): 1 hour, 6 hours, and 12 hours, Sample 9: 15 minutes, 30 minutes, 1 hour. The time intervals chosen appeared to have the most transferred material present on the cotton swatches for each of these samples. All three of the cuttings were added to a vial containing 500 µl of acetone and vortexed for approximately 3 minutes. The supernatant was analyzed using the same GC-MS methods as the commercial products, DHA6.

All of the GC-MS data was analyzed using Agilent ChemStation and then compared with one another.
4. RESULTS AND DISCUSSION

4.1. VISUAL EXAMINATION

The general physical descriptions of each commercial product varied greatly. Apart from the difference in application type for each commercial product, lotion, spray, foam, or towelette, there were several differences seen in the color and presence of lustrous pigmentation (sparkle) among samples of each type. Colors varied from a shiny white, to a sparkling orange, to a dark brown.

Given that there was a difference in the physical characteristics of each of the samples, it was expected that each of these samples would also produce varying results when transferred onto a white cotton swatch. The variation between each sample on white cotton can be seen in Figure 4. Samples 1-16 added directly to cotton swatch. For many of the commercial samples that were labeled as “instant action” (samples 2, 3, 5, 7, 9, 15, 16), a brown-orange color was immediately visible on the cotton upon application. Four of the samples (10, 11, 12, 14) were intended to show a color change on the skin within 2-3 hours after application according to the manufacturers22–25. When added to the cotton, there were no stains visible for these four samples. This suggests that these samples do not have a bronzing additive and the color change only becomes visible after the DHA in each of these samples reacts with the amino acids on the skins surface. This observation was also true for the "gradual tan" samples (samples 1, 4, 6, 8, 13). For some of the samples, a faint yellow-cream colored stain was visible. This
may be due to other components within the product, as the color of these samples were yellow-cream to start.

Figure 4. Samples 1-16 added directly to cotton swatch.

Observations made under different light sources also displayed variations between the samples (Table 3). The stereoscope allowed the visualization of the lustrous particles that create the shimmer or sparkle in the product on the surface of the fabric’s fibers. These lustrous particles were present on samples 2, 3, 5, and 15. This characteristic was also visible in the liquid commercial samples and immediately after the product was applied to the skin. The only sample that did not display lustrous particles on the fabric that were present in the liquid commercial sample and on the skin was sample 16, the Vita Liberata foaming mousse.
All of the samples displayed varying colors and degrees of fluorescence under 455 nm and 535 nm light sources. While the color of the fluorescence is not indicative of a sample’s identity, it can aid an analyst in locating stains, which may otherwise go unnoticed and it is useful to note that some of these commercial products can go undetected, even with the use of an alternate light source.

Table 3. Observed results of samples visualized under white light, a stereoscope and at 455 nm and 535 nm.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Description of Sample on Cotton</th>
<th>White Light</th>
<th>Stereoscope</th>
<th>455 nm</th>
<th>535 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>2. L’Oreal Paris Sublime Bronze Luminous Bronzer Self-Tanning Lotion</td>
<td>Bronze/orange sparkly stain. Color visible on front and back. Sparkles only visible on side of application.</td>
<td>Color appears more brown. Sparkle particles loose on surface of fibers of application side only.</td>
<td>Bright White Fluorescent Stain</td>
<td>Bright Orange Stain</td>
<td></td>
</tr>
<tr>
<td>3. L’Oreal Paris Sublime Bronze Natural Tinted Self-Tanning Lotion</td>
<td>Bronze/orange sparkly stain. Color visible on front and back. Sparkles only visible on side of application.</td>
<td>Color appears more tan. Sparkle particles loose on surface of fibers of application side only.</td>
<td>Bright White Fluorescent Stain</td>
<td>Bright Orange Stain</td>
<td></td>
</tr>
<tr>
<td>5. CVS Sunless Tinted Lotion</td>
<td>Light brown/orange stain. Color visible on front and back. Sparkles visible on side of application only.</td>
<td>Color appears more tan. Sparkle particles are loose on fibers of application side only.</td>
<td>Bright White Fluorescent Stain</td>
<td>Bright Orange Stain</td>
<td></td>
</tr>
<tr>
<td>6. Jergen’s Natural Glow Revitalizing Daily Moisturizer</td>
<td>Faint yellow stain visible on both front and back, but lighter on back side. Fabric’s fibers appear unaltered.</td>
<td>Faint yellow stain visible on both front and back, but lighter on back side. Fabric’s fibers appear unaltered.</td>
<td>Faint White Fluorescent Stain</td>
<td>No Stain Visible</td>
<td></td>
</tr>
<tr>
<td>Sample Name</td>
<td>White Light</td>
<td>Stereoscope</td>
<td>455 nm</td>
<td>535 nm</td>
<td></td>
</tr>
<tr>
<td>-------------</td>
<td>-------------</td>
<td>-------------</td>
<td>--------</td>
<td>--------</td>
<td></td>
</tr>
<tr>
<td>10. L’Oreal Paris Sublime Bronze ProPerfect Salon Mist</td>
<td>No stain visible.</td>
<td>No stain visible.</td>
<td>Faint White Fluorescent Stain</td>
<td>No Stain Visible</td>
<td></td>
</tr>
<tr>
<td>15. St. Tropez One Night Only: Instant Glow Body Lotion</td>
<td>Dark brown stain visible on front and back with minimal sparkle visible on the side of application.</td>
<td>Dark brown stain visible on front and back. Sparkle particles loose on fabric's fibers.</td>
<td>Red Fluorescent Stain</td>
<td>Very Bright Dark Orange Stain</td>
<td></td>
</tr>
<tr>
<td>16. Vita Liberata Tinted Self Tan Mousse for Body</td>
<td>Multicolored stain visible on both sides-red/orange center, orange/brown/yellow middle, green outer ring. No sparkle.</td>
<td>Multicolored stain visible on both sides-red/orange center, orange/brown/yellow middle, green outer ring. No sparkle.</td>
<td>Orange Fluorescent Stain</td>
<td>Bright Orange Stain</td>
<td></td>
</tr>
</tbody>
</table>
4.2. SOLUBILITY

The solubility of each sample was tested in methanol, acetone, and ethyl acetate. It was found that the greatest number of samples (11) were fully soluble in acetone, with the remaining 5 samples being partially soluble. These results are consistent with what was expected given that the chemical structure of acetone and DHA are very similar, both being ketones.

Both methanol and ethyl acetate were unable to solubilize some of the samples. For this reason, acetone was chosen as the solvent of choice for extractions in the remainder of the study. The results of the solubility tests can be seen in Table 4.
Table 4. The solubility of each sample in methanol, acetone, and ethyl acetate

<table>
<thead>
<tr>
<th>Sample</th>
<th>Methanol</th>
<th>Acetone</th>
<th>Ethyl Acetate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Olay Body Quench Plus Touch of Sun</td>
<td>White Precipitate, partially soluble</td>
<td>Soluble</td>
<td>Stayed on swab, insoluble</td>
</tr>
<tr>
<td>L’Oreal Sublime Bronze Luminous Bronzer</td>
<td>White Precipitate, partially soluble</td>
<td>Soluble</td>
<td>Stayed on swab, insoluble</td>
</tr>
<tr>
<td>L’Oreal Sublime Bronze Tinted Self-Tanning</td>
<td>Soluble</td>
<td>Soluble</td>
<td>Soluble</td>
</tr>
<tr>
<td>Coppertone Sunless Gradual Tan</td>
<td>White Precipitate, partially soluble</td>
<td>White Precipitate, partially soluble</td>
<td>Soluble</td>
</tr>
<tr>
<td>CVS Sunless Tinted Lotion</td>
<td>White Precipitate, partially soluble</td>
<td>White Precipitate, partially soluble</td>
<td>Stayed on swab, insoluble</td>
</tr>
<tr>
<td>Jergen’s Natural Glow 3 Day to Glow</td>
<td>Soluble</td>
<td>White Precipitate, partially soluble</td>
<td>Soluble</td>
</tr>
<tr>
<td>Banana Boat Summer Color Self- Tanning Lotion</td>
<td>White Precipitate, partially soluble</td>
<td>White Precipitate, partially soluble</td>
<td>Large, clumpy precipitate, insoluble</td>
</tr>
<tr>
<td>Neutrogena Build-a-Tan</td>
<td>White Precipitate, partially soluble</td>
<td>Soluble</td>
<td>Soluble</td>
</tr>
<tr>
<td>Equate Beauty Self Tan Bronzing</td>
<td>Soluble</td>
<td>Dark precipitate at bottom, partially soluble</td>
<td>Liquid bi-layer</td>
</tr>
<tr>
<td>L’Oreal Sublime Bronze Self- Tanning Spray</td>
<td>Soluble</td>
<td>Soluble</td>
<td>Liquid bi-layer</td>
</tr>
<tr>
<td>Neutrogena MicroMist</td>
<td>Soluble</td>
<td>Soluble</td>
<td>Liquid bi-layer</td>
</tr>
<tr>
<td>Banana Boat Summer Color Self- Tanning Spray</td>
<td>Soluble, but cloudy</td>
<td>Soluble</td>
<td>Liquid bi-layer</td>
</tr>
<tr>
<td>Jergen’s Natural Glow Daily Foam</td>
<td>Soluble</td>
<td>Soluble</td>
<td>Insoluble</td>
</tr>
<tr>
<td>L’Oreal Sublime Bronzing Towelettes</td>
<td>Soluble, but cloudy</td>
<td>Soluble</td>
<td>Small, clear precipitate, partially soluble</td>
</tr>
<tr>
<td>St. Tropez Instant One Night Only Lotion</td>
<td>Sparkles precipitated out, suspended in solution, partially soluble</td>
<td>Soluble</td>
<td>Stayed on swab, Insoluble</td>
</tr>
<tr>
<td>Vita Liberata Tanning Mousse</td>
<td>Soluble</td>
<td>Soluble</td>
<td>Stayed on swab, Insoluble</td>
</tr>
</tbody>
</table>

4.3. SAMPLING METHOD UTILIZED

Scrapping the samples off of the cotton swatches using a scalpel blade provided the greatest yield of product as well as the most reproducible FTIR
spectra. Furthermore, this was the quickest and most convenient technique. The scraping method was adopted for the extraction and sampling of all products in the study and were analyzed on the diamond compression cell with the microscope attachment in the FTIR.

4.4. TRANSFER STUDY

The transfer of sunless self-tanner at each of the assigned time intervals was photographed and the observations were recorded. Each of the transferred samples can be seen in Table 5. All of the sixteen commercial samples tested in this study transferred from skin onto the cotton swatches. Samples 1, 4, 6, 7, 8, and 13 were labeled by the manufacturers as gradual sunless self-tanners and were tested after one application (1X) and after three consecutive days of application (3X), bringing the total number of sunless self-tanner samples tested in the transfer study to 22.
Table 5. Photographs of each transferred consumer product sample from skin onto cotton at 15 minutes, 30 minutes, 1 hour, 3 hours, 6 hours, and 12 hours after application. Samples that were intended to produce a gradual tan over multiple applications

<table>
<thead>
<tr>
<th>Sample</th>
<th>15 min</th>
<th>30 min</th>
<th>1 hr</th>
<th>3 hr</th>
<th>6 hr</th>
<th>12 hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Olay Body Quench Plus Touch of Sun (1X)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. Olay Body Quench Plus Touch of Sun (3X)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2. L’Oreal Sublime Bronze Luminous Bronzer⁴</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3. L’Oreal Sublime Bronze Tinted Self-Tanning</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4. Coppertone Sunless Gradual Tan (1X)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4. Coppertone Sunless Gradual Tan (3X)</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>5. CVS Sunless Tinted Lotion</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample</td>
<td>15 min</td>
<td>30 min</td>
<td>1 hr</td>
<td>3 hr</td>
<td>6 hr</td>
<td>12 hr</td>
</tr>
<tr>
<td>-----------------------------------------------------------------------</td>
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</tr>
<tr>
<td>6. Jergen's Natural Glow 3 Day to Glow (1X)</td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>6. Jergen's Natural Glow 3 Day to Glow (3X)</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>7. Banana Boat Summer Color Self-Tanning Lotion (1X)</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>7. Banana Boat Summer Color Self-Tanning Lotion (3X)</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>8. Neutrogena Build-a-Tan (1X)$^2$</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8. Neutrogena Build-a-Tan (3X)$^2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9. Equate Beauty Self Tan Bronzing</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10. L'Oreal Sublime Bronze Self-Tanning Spray</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample</td>
<td>15 min</td>
<td>30 min</td>
<td>1 hr</td>
<td>3 hr</td>
<td>6 hr</td>
<td>12 hr</td>
</tr>
<tr>
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<td>--------</td>
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<td>------</td>
<td>------</td>
<td>-------</td>
</tr>
<tr>
<td>11. Neutrogena MicroMist²</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
</tr>
<tr>
<td>12. Banana Boat Summer Color Self-Tanning Spray</td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
<td><img src="image9.png" alt="Image" /></td>
<td><img src="image10.png" alt="Image" /></td>
<td><img src="image11.png" alt="Image" /></td>
<td><img src="image12.png" alt="Image" /></td>
</tr>
<tr>
<td>13. Jergen's Natural Glow Daily Foam (1X)</td>
<td><img src="image13.png" alt="Image" /></td>
<td><img src="image14.png" alt="Image" /></td>
<td><img src="image15.png" alt="Image" /></td>
<td><img src="image16.png" alt="Image" /></td>
<td><img src="image17.png" alt="Image" /></td>
<td><img src="image18.png" alt="Image" /></td>
</tr>
<tr>
<td>13. Jergen's Natural Glow Daily Foam (3X)</td>
<td><img src="image19.png" alt="Image" /></td>
<td><img src="image20.png" alt="Image" /></td>
<td><img src="image21.png" alt="Image" /></td>
<td><img src="image22.png" alt="Image" /></td>
<td><img src="image23.png" alt="Image" /></td>
<td><img src="image24.png" alt="Image" /></td>
</tr>
<tr>
<td>14. L'Oreal Sublime Bronzing Towelettes</td>
<td><img src="image25.png" alt="Image" /></td>
<td><img src="image26.png" alt="Image" /></td>
<td><img src="image27.png" alt="Image" /></td>
<td><img src="image28.png" alt="Image" /></td>
<td><img src="image29.png" alt="Image" /></td>
<td><img src="image30.png" alt="Image" /></td>
</tr>
<tr>
<td>15. St. Tropez Instant One Night Only Lotion¹</td>
<td><img src="image31.png" alt="Image" /></td>
<td><img src="image32.png" alt="Image" /></td>
<td><img src="image33.png" alt="Image" /></td>
<td><img src="image34.png" alt="Image" /></td>
<td><img src="image35.png" alt="Image" /></td>
<td><img src="image36.png" alt="Image" /></td>
</tr>
<tr>
<td>16. Vita Liberata Tanning Mousse</td>
<td><img src="image37.png" alt="Image" /></td>
<td><img src="image38.png" alt="Image" /></td>
<td><img src="image39.png" alt="Image" /></td>
<td><img src="image40.png" alt="Image" /></td>
<td><img src="image41.png" alt="Image" /></td>
<td><img src="image42.png" alt="Image" /></td>
</tr>
</tbody>
</table>

¹Cuttings from these samples were used in the testing of extraction methods
²These samples were initially lighter in color at the time of transfer and then darkened on the cotton over time.
Eleven of the samples showed consistent amounts of transferred material across all six of the time intervals as seen in Table 5 and Table 6. This suggests that the samples do not transfer in a time dependent manner, but rather deposit a relatively similar amount of material onto the cotton swatches regardless of how long the product has been on the skin prior to the transfer. Three of the samples transferred less material over time, and six samples transferred more material as time increased since application.

Table 6. Summary of color intensity as time since application increased. The amount/color intensity of tanner transferred onto the cotton either (A) remained the same, (B) decreased, or (C) increased as the time since application increased.

<table>
<thead>
<tr>
<th>Amount of Transferred Tanner Over Time</th>
<th>Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Remained the same</td>
<td>1(1X), 1(3X), 2, 4(1X), 6(1X), 7(3X), 10, 12, 13(1X), 13(3X), 14</td>
</tr>
<tr>
<td>B. Decreased</td>
<td>7(1X), 9, 15</td>
</tr>
<tr>
<td>C. Increased</td>
<td>3, 4(3X), 5, 6(3X), 8(1X), 8(3X), 11, 16</td>
</tr>
</tbody>
</table>
amount of transferred material. These observations may not be indicative of the quantity of the material transferred onto the cotton. Some products were intended to produce a medium/dark tan while others were intended to produce a light tan, or were intended for a lighter skin tone, which may have affected the intensity of the color seen on the cotton swatches as well. Therefore, the color intensities should not be used to compare the amount of transferred material between products, but can be helpful to compare the amount of transferred material across time intervals for a single product.

4.5. FTIR ANALYSIS

FTIR analysis of the commercial products prepared directly from their bottles produced similar spectra (Figure 6) apart from sample 15, seen in orange. The more notable absorption peaks in the other 15 samples were an O-H stretch around 3300 cm\(^{-1}\) and a C=C alkene stretch around 1650 cm\(^{-1}\). Some differences were seen at approximately 1100 cm\(^{-1}\), however, overall the spectra of these 15 samples were remarkably similar.
Figure 6. Overlay of IR spectra of all 16 commercial products added directly to a cotton swatch

The DHA standard (Figure 7) displayed strong absorption peaks at 3450 and 3398.2 cm\(^{-1}\) indicative of an O-H stretch, and at 1071.4 cm\(^{-1}\) indicative of a C-O stretch. Evidence of a sp3 C-H stretch can be seen at 3142.2 cm\(^{-1}\) and an O-H bend at 968.3 cm\(^{-1}\).
The FTIR spectrum of a cotton swatch that had wiped unaltered skin (Figure 8) was subtracted from the spectra for each sample. Each of the resulting spectra showed similar absorption peaks with strong sp3 and sp2 C-H absorption peaks around 2800 cm\(^{-1}\). A strong C-O stretch was seen in most spectra at approximately 1050 cm\(^{-1}\) and a strong C=O stretch at approximately 1650 cm\(^{-1}\). An O-H stretch was also seen in most of the spectra at approximately 3300 cm\(^{-1}\). The similarities seen between these spectra may indicate that the many sunless self-tanners are comprised of several of the same ingredients. Appendix A shows the individual resulting IR spectra of the transferred sunless self-tanner samples taken from the cotton swatches.
Each of the sunless self-tanners are composed of numerous different ingredients, each of which are exposed to the IR beam and responding to the energy source. This may contribute to the amount of absorption peaks seen across all different wavelengths. The complexity of each of these spectra makes it difficult to individualize each of the commercial products from one another. There were some small differences between spectra which allowed the sixteen samples to be grouped based on their similarities (Table 7). The six groups differ primarily in the fingerprint region of the spectra.
Table 7. Grouped samples that displayed visually similar absorption peaks when analyzed using FTIR

<table>
<thead>
<tr>
<th>Sample</th>
<th>1, 4, 6, 7, 8, 12, 13, 14</th>
</tr>
</thead>
<tbody>
<tr>
<td>Group A</td>
<td>2, 3, 5</td>
</tr>
<tr>
<td>Group B</td>
<td>10, 11</td>
</tr>
<tr>
<td>Group C</td>
<td>9</td>
</tr>
<tr>
<td>Group D</td>
<td>15</td>
</tr>
<tr>
<td>Group E</td>
<td>16</td>
</tr>
</tbody>
</table>

Group A, containing samples 4, 6, 8, 12, 13, and 14, showed strong absorption peaks around 3300 cm\(^{-1}\), 2852-2925 cm\(^{-1}\), and 1100 cm\(^{-1}\). A weak absorption peak was seen at 2358 cm\(^{-1}\) as well as medium intensity peaks at 1719-1733 cm\(^{-1}\), 1619-1666 cm\(^{-1}\), 1585-1591 cm\(^{-1}\), 1452-1462 cm\(^{-1}\), 1351-1398 cm\(^{-1}\), 1240-1276 cm\(^{-1}\), 714-721 cm\(^{-1}\). Five of the eight samples in this group were labeled as gradual tanners, which may have attributed to the similarities seen in the spectra. The group contained all four of the application types: lotion, foam, spray, and towelette. This suggests that the application type cannot be determined using FTIR.

Group B, samples 2, 3, and 5, differed from the other spectra in that all three lacked the absorption peaks seen at 2358 cm\(^{-1}\), 1585-1591 cm\(^{-1}\), 1100 cm\(^{-1}\), and 714-721 cm\(^{-1}\). There were absorption peaks in this group that appeared similar to
peaks seen in Group A, however the peaks were seen at slightly lower wavelengths, differing from the peaks of Group A by approximately 50-75 cm\(^{-1}\). The peaks seen were at 1543-1551 cm\(^{-1}\) and 1030-1043 cm\(^{-1}\). The three sunless self-tanner samples in this group were all lotions and were all visually similar. Two of the samples were L’Oreal Sublime Bronze self-tanners and the third was a generic CVS brand lotion that claimed to be comparable to the L’Oreal Sublime Bronze product line.

Both Group A and Group B showed similar spectra to the unaltered skin. The five notable absorption peaks seen in the spectrum of the unaltered skin at 3275.1 cm\(^{-1}\), 2917 cm\(^{-1}\), 2849.5 cm\(^{-1}\), 1650 cm\(^{-1}\), and 1547 cm\(^{-1}\) were also seen in spectra of both of these groups, particularly in samples 1, 7 (1X), and 13 (3X) of Group A and samples 3 and 5 of Group B. All of these spectra had additional peaks of lower intensities between 700 and 1500 cm\(^{-1}\), however, the more notable peaks seen in the spectra made them remarkably similar to the spectrum of the unaltered skin. There was no correlation apparent in the amount of transferred self-tanner that could visually be seen on the cotton swatches in these samples that produced similar spectra to the unaltered skin.

Group C contained samples 10 and 11. These two samples both lacked the absorption peaks at 1585-1591 cm\(^{-1}\) and 1543-1551 cm\(^{-1}\). Additionally, there were no peaks seen past 1080 cm\(^{-1}\). Both of these samples were misting sprays. Like samples in Group A and Group B, sample 11 showed similar absorption peaks to the unaltered skin.
The follow three groups each contain one sample. Group D, sample 9, showed medium intensity peaks at 3236 cm\(^{-1}\) and 2860 cm\(^{-1}\). This spectrum also displayed a strong absorption peak at 2357 cm\(^{-1}\). The fingerprint region displayed five strong absorption peaks at 1827 cm\(^{-1}\), 1627 cm\(^{-1}\), 1522 cm\(^{-1}\), 1398 cm\(^{-1}\), 1231 cm\(^{-1}\), and 1080 cm\(^{-1}\). Like group C, there were no peaks seen past 1080 cm\(^{-1}\). Sample 9 was visually very different from the other samples. Unlike all of the other misting sprays which were colorless, sample 9 was green in color.

Group E, sample 15, displayed the most unique spectrum. This spectrum displayed strong absorption peaks at 3225 cm\(^{-1}\), 1679 cm\(^{-1}\), 1167 cm\(^{-1}\), and 1030 cm\(^{-1}\). Other weaker intensity peaks were seen at 1679 cm\(^{-1}\), 1614 cm\(^{-1}\), 1561 cm\(^{-1}\), 1447 cm\(^{-1}\), 1354 cm\(^{-1}\), and 1300 cm\(^{-1}\). This unique spectrum matched the uniqueness of the tanning product itself. This sample was the only sample that did not contain DHA. The product was intended to produce a tanned appearance for one night only, rather than dying the skin for a longer time period. It was expected that this sample would produce a slightly different spectrum from the rest of the samples due to the lack of the key tanning ingredient.

The last group contains sample 16. It differed in that it displayed peaks at 2108 cm\(^{-1}\), 1588 cm\(^{-1}\), and 1187 cm\(^{-1}\), and lacked peaks seen in many of the other spectra. This sample claimed to use all natural and organic products. It also was visually different from the other samples in both white light and when observed on cotton under an alternate light source (Table 3). In comparison to the other foaming
self-tanner, sample 13, which was a thick white mousse, sample 16 was an aerated brown lustrous foam.

Overall the spectra of each of the samples showed many similarities, however, small differences observed allowed the spectra to be separated into six groups that showed similar absorptions. It was difficult to individualize the samples further and it was not possible to distinguish between application types using FTIR analysis given that all four of the application types produced similar spectra seen in Group A. While the FTIR may not be sensitive enough to differentiate between the products, it is just as important to note that each sample is likely to produce a relatively similar spectrum, which may help an analyst identify an unknown stain as a sunless self-tanner as opposed to another cosmetic product. For example, while other cosmetic products, such as foundation or blush, may appear similar on a fabric swatch, the IR spectra may differ from the sunless self-tanner spectra.

4.6 ANALYSIS OF SAMPLES USING GC-MS

4.6.1. ANALYSIS OF SAMPLES PREPARED DIRECTLY FROM THEIR PACKAGING

It was difficult to differentiate between samples using the FTIR, however, there was some success in classifying the samples into groups based on similarities between spectra. GC-MS analysis proved to be more successful in separating and identifying the components of each of the samples. There were
several chemical ingredients that were shared by each of the samples, yet there were also chemical ingredients present that were unique to each sample. DHA was seen at an average retention time of 6.167 minutes in all samples except for Sample 15: St. Tropez One Night Only- Instant Body Lotion. The lack of DHA in this sample was expected given that this product, as the name implies, is intended to provide a tan for a short period of time and then wash off during bathing\textsuperscript{26}. Glycerin was identified in all of the samples, eluting off the column at an average retention time of 6.701 minutes. Other ingredients such as cholestane, which is used as an antioxidant\textsuperscript{27}, and methylparaben, used to prevent and retard bacterial and fungal growth and subsequently increase the shelf life of the product\textsuperscript{28–30}, were also seen in the majority of the products.

There are several chemical ingredients that are consistent between the commercial products tested, yet there were also several peaks present that were unique to each of the samples allowing the differentiation between products, and even between products of the same brand, as seen in Figure 9, Figure 10, and Figure 11. β-hydroxyethyl phenyl ether, more commonly known as aerosol, was identified in all four of the spray products (Samples 9-12: Equate Beauty Self-Tanning Spray, L’Oreal Sublime Bronze Spray, Neutrogena MicroMist, and Banana Boat Summer Color Spray) as well as in Sample 16: Vita Liberata Foaming Mousse. Also, a peak identified as methoxyacetic acid was seen in some of the samples that were labeled “instant action” (Sample 2: L’Oreal Sublime Bronze, Sample 3: L’Oreal Sublime Bronze Luminous, and Sample 5: CVS Sunless
Tanner). Each of these three samples contain caramel coloring which allowed for an instant color change upon application. Methoxyacetic acid is a banned additive in cosmetics in the European Union,\textsuperscript{19} as it has been documented to contribute to fertility impairments as well as lead to possible damage to unborn children\textsuperscript{31} however, it is still used in the United States as both a fragrance\textsuperscript{32} and as a coloring agent\textsuperscript{33}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{comparison_of_four_loreal_samples.png}
\caption{Chromatogram comparing four L’Oreal Paris Sublime Bronze products: L’Oreal Bronze Self-Tanning Spray (orange), L’Oreal Sublime Bronze Luminous Lotion (grey), L’Oreal Sublime Bronze Tinted Tanning Lotion (yellow), L’Oreal Sublime Bronze Towelettes (blue)}
\end{figure}
Figure 10. Chromatogram comparing two Banana Boat Summer Color products: Banana Boat Summer Color Lotion (blue) and Banana Boat Summer Color Misting Spray (Orange)

Figure 11. Chromatogram comparing two Jergen's Natural Glow products: Jergen's Natural Glow Foaming Moisturizer (blue) and Jergen's Natural Glow Lotion (orange)
Chemical ingredients such as glycerin, acetic acid, and acetone, were seen in the majority of the sample. There were also several chemical ingredients that differed between products, many of which were used to scent the sunless self-tanners, such as linalool, cinnamaldehyde, and linalyl anthranilate. Some of the ingredients that were detected using the GC-MS are listed in Table 8.
Table 8. Results of GC-MS analysis: List of peaks identified in each of the 16 samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
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<th>16</th>
</tr>
</thead>
<tbody>
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</tr>
<tr>
<td>Dipropylene Glycol</td>
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<td>X</td>
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<td>Linalyl Anthranilate</td>
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<td>β- Hydroxyethyl PhenyI Ether</td>
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<td>Benzoic acid</td>
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<td>Glyceraldehyde</td>
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<td>Musk</td>
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</table>
There was no one ingredient that was able to differentiate one sunless self-tanner from another, however, a combination of some of the identified peaks was able to differentiate the samples. A list of peaks that were unique to each of the samples can be seen in Table 9.

Table 9. List of unique chemical ingredients found in each of the 16 samples using GC-MS analysis

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Sample Name</th>
<th>Chemical Ingredient</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Olay Quench Plus Touch of Sun Body Lotion, Light/Medium Skin Tones</td>
<td>1. Aluminum starch octenyl succinate</td>
</tr>
</tbody>
</table>
| 2             | L’Oreal Paris Sublime Bronze Luminous Bronzer Self-Tanning Lotion | 1. Methoxyacetic acid  
2. Methyl dihydrojasminite  
3. Dihydromyrcenol |
| 3             | L’Oreal Paris Sublime Bronze Natural Tinted Self-Tanning Lotion | 1. Ocinaene  
2. Soybean Oil  
3. Lycoxanthin |
| 4             | Coppertone Endless Summer, Gradual Tanning Lotion       | 1. Faresence  
2. Eugenol  
3. Piperonal  
4. Lycopene |
| 5             | CVS Sunless Tinted Lotion                               | 1. Azulenone  
2. Coridendrin  
3. Lycoxanthin |
| 6             | Jergen’s Natural Glow Revitalizing Daily Moisturizer, Medium/Tan Skin Tone | 1. Beta Fluorine  
2. Hydroxyethyl acetate  
3. Propyl cyclohexanol |
| 7             | Banana Boat Summer Color Self-Tanning Lotion            | 1. Allyl heptanoate  
2. Oxazolidine  
3. Vertenex  
4. Dihydromyrcenol  
5. Cis-geraniol  
6. m-pyrol  
7. Undecyl ether |
| 8             | Neutrogena Build-a-Tan Gradual Sunless Tanning Lotion    | 1. Methylygaxal  
2. Cis-geraniol  
3. Butylated Hydroxytoluene  
4. Anisaldehyde  
5. Coridendrin  
6. Cyclamal  
7. Amysaliculate  
8. Neroline yara yara |
| 9             | Equate Beauty Flawless Self-Tan Bronzing Spray          | 1. Camphor  
2. Octadienol |
Each commercial sample displayed a unique set of peaks and chemical ingredients that could potentially help identify the brand of product if it was probative in a forensic investigation. Many of the peaks that were unique to each sample were low in abundance, therefore it is important to analyze the entire chromatogram in order to make a more accurate identification. Each of the peaks identified provide a separate role in the overall composition of the sunless Tanner. For example, Laureth-1 and Laureth-2, found in samples 12, 13, and 14, are both

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Sample Name</th>
<th>Chemical Ingredient</th>
</tr>
</thead>
</table>
| 10            | L’Oreal Paris Sublime Bronze ProPerfect Salon Airbrush Self-Tanning Mist-Medium Natural Tan | 1. Propynol-1,1-oxybis  
                                    2. β-Hydroxyethyl Phenyl Ether |
| 11            | Neutrogena Micro Mist Airbrush Sunless Tan                                    | 1. Carbitol  
                                    2. Bergamol  
                                    3. β-Hydroxyethyl Phenyl Ether  
                                    4. Isosorbide dimethyl ether |
| 12            | Banana Boat Summer Color Self-Tanning Mist                                   | 1. p-Cymene  
                                    2. Benzhydrazide  
                                    3. Laureth-2  
                                    4. β-Hydroxyethyl Phenyl Ether |
| 13            | Jergen’s Natural Glow Lightweight Foaming Daily Moisturizer                  | 1. DLG  
                                    2. Laureth-1 |
| 14            | L’Oreal Paris Sublime Bronze Self-Tanning Towelettes, Medium Natural Tan    | 1. p-cymene  
                                    2. Dihydromyrcenol  
                                    3. Acetylaldehyde  
                                    4. Antar (octyl ether)  
                                    5. Laureth-1  
                                    6. Myristyl monoethoxylate  
                                    7. Laureth-2 |
| 15            | St. Tropez One Night Only: Instant Glow Body Lotion                          | 1. Isocetane  
                                    2. Pantolacetone  
                                    3. Canthaxanthin  
                                    4. Absence of DHA |
| 16            | Vita Liberata Tinted Self Tan Mousse for Body                                | 1. Oxylic Acid  
                                    2. Sorbic acid  
                                    3. β-Hydroxyethyl Phenyl Ether |
compounds that fall under the category of anionic detergents that are often added to personal care products. Sodium laureth sulfates are particularly good foaming agents. When added to cosmetics, Laureth-1 and Laureth-2 are typically used as emulsifying agents\cite{34}. Dihydromyrcenol, in samples 2, 7, and 14, and p-cymene, in samples 12 and 14, add a citrus fragrance additive in topical cosmetics that also provides antifungal properties\cite{35,36}. Similarly, sorbic acid, in sample 16, is added to personal care products as an anti-microbial agent\cite{37}.

![Chemical structure of Laureth](image)

*Figure 12. Chemical structure of Laureth*

![Chemical structure of p-cymene, dihydromyrcenol and Sorbic acid](image)

*Figure 13. Chemical structure of p-cymene (left), dihydromyrcenol (center) and Sorbic acid (right)*
Figure 14. A portion of the chromatogram of Sample 14: L’Oreal Sublime Bronze Towelette with peak (A) p-cymene and (B) dihydromyrcenol

Figure 15. A portion of the chromatogram of Sample 14: L’Oreal Sublime Bronze Towelette with peak (A) Laureth-1 and (B) Laureth-2
One of the more unique ingredients that was identified by GC-MS analysis was canthaxanthin ($C_{40}H_{52}O_2$), the active tanning agent in Sample 15: St. Tropez One Night Only Glow Body Lotion. This terpenoid is an organic pigment that is often added to both foods and cosmetics\textsuperscript{18}. Canthaxanthin is a legal additive in the United States and the United Kingdom, but has been banned in Australia and New Zealand due to potential retinal damage\textsuperscript{18,38,39}. While canthaxanthin is still legal as a topical ingredient in some countries, it is no longer used in the form of an oral tanning pill as it once was\textsuperscript{18,38}.

![Chemical Structure of canthaxanthin](image)

\textit{Figure 16. Chemical Structure of canthaxanthin}

### 4.6.2. ANALYSIS OF TRANSFERRED MATERIAL ON WHITE COTTON SWATCHES

Analysis of the transferred material on white cotton swatches was performed on two samples, Sample 7: Banana Boat Summer Color Self-Tanning Lotion and Sample 9: Equate Beauty Flawless Self-Tan Bronzing Spray. The samples were compared to the chromatograms of the samples when prepared directly from their bottles/packaging. For each of these samples, peaks were identified in the transferred samples that were also seen in the reference chromatograms as seen in Figure 17 and Figure 18.
Figure 17. Chromatograms of Sample 7 obtained from transferred material on a cotton swatch (top) and the product prepared for analysis directly from the bottle (bottom). A-D mark shared peaks between the two chromatograms (A: propylene glycol, B: hexadecen-1-ol, trans-9-, C: hexadecanoic acid, D: cholestane)
There were four peaks identified in the chromatogram of the transferred material from sample 7 that were also seen in the sample when prepared directly from the product bottle (Figure 17). The peaks were identified as the following: A: propylene glycol, a chemical ingredient that serves as a hydrophilic vehicle providing hydration to the cosmetic\(^4\); B: hexadecen-1-ol, trans-9-, which serves as an emulsifier for the cosmetic product\(^4\); C: hexadecanoic acid, found in palm oil\(^4\), and D: cholestane, an essential oil found in hemp, which provides both fragrance and moisturizing effects for the cosmetic\(^4\) as well as antioxidant properties\(^4\). DHA was not seen in the chromatogram of the transferred material, nor was \(\beta\)-hydroxyethyl phenyl ether (aerosol). The absence of these two chemical ingredients may be due to their volatility. Both compounds are small, volatile compounds that may evaporate off of the skin as the product dries. Also, because DHA reacts with the stratum corneum layer of the skin, it is possible that when the chemical penetrates this skin layer and reacts with the amino acids it changes its chemical makeup and may become more difficult to transfer from the skin in comparison to other components of the sunless self-tanner.
Figure 18. Chromatogram of the transferred material of sample 9 (top) and of sample 9 when prepared directly from the product bottle. A-D mark shared peaks between the two samples. A: propylene glycol, B: 1-heptadecanol, C: hexadecen-1-ol, trans-9-, D: cholestane
There were four peaks identified in the transferred material of sample 9 that were also seen in the sample when prepared directly from the bottle (Figure 18). The peaks were identified as the following: A: propylene glycol, a hydrophilic vehicle\textsuperscript{40}, B: the active tanning ingredient, DHA, and C: 1-heptadecanol and D: hexadecan-1-ol, trans-9-, both emulsifying agents\textsuperscript{30,40,41}. The peak for DHA, seen at a retention time of 6.107 minutes, was extremely small in comparison to the product prepared directly from the bottle where it was the most abundant peak at an abundance of $5,022,428$. The abundance of the DHA in the transferred sample was $155,307$. Similar to the transferred material of sample 7, the absence or low abundance of some of the chemical ingredients that were seen in the product may be due to the volatility of these compounds or reactions that occur post application to the skin.

For both sample 7(3X) and sample 9, the peaks identified in the material transferred onto cotton swatches did not match any of the chemical ingredients that were previously labeled as unique components of the product when prepared directly from the packaging. It is possible however, even with the absence of some of these unique peaks to identify transferred samples on clothing as a sunless self-tanner if a known product is available for comparison. Therefore, a known sunless self-tanner found in an individual’s home could be analyzed and compared to suspected sunless-tanner-stained items of evidence.
5. CONCLUSION

Regardless of the information provided by health organizations on the risks of UV exposure, a tanned appearance is still considered attractive and is sought out by several individuals. Due to increased awareness of the health risks, cosmetic companies have made sunless self-tanners available, providing a tanned appearance without the requirement of harmful UV exposure. The color change of the skin produced by sunless self-tanners is due to a small, polar molecule known as dihydroxyacetone (DHA). DHA is a colorant that reacts with the amino acids in the stratum corneum (SC), the outer most layer of the skin, to produce a brown semi-permanent color change.

While the sunless self-tanners have improved greatly in their overall quality, the products are still known to transfer onto the wearer's clothing despite claims made by the manufacturers. While this is a highly undesirable characteristic for the consumer, the product’s ability to transfer onto clothing makes sunless self-tanners a valuable piece of forensic evidence in cases where an altercation between two individuals has occurred, specifically in violent attacks such as sexual assaults, beatings, or homicides. The presence of sunless self-tanner on an individual’s clothing could help corroborate a story and certainly provide additional pieces of evidence and leads in an investigation.

The purpose of this study was to first determine if sunless self-tanners that are readily available to consumers transfer from skin to clothing, a characteristic that would go against the manufacturer’s claim of being a transfer free product.
Given that a transfer of the sunless self-tanners occurs, this research was also intended to both detect and discriminate between different self-tanning products using instrumental techniques that would typically be used in forensic labs.

All of the sixteen sunless self-tanners tested transferred from the skin onto a white 4 inch by 4 inch cotton swatch when forcibly wiped at each time interval. Of the 22 samples (includes both the one time (1X) and three time (3X) application samples of the gradual sunless self-tanners) tested, eleven the samples displayed a consistently similar amount of transferred material across all six times frames since application. Three samples transferred less material onto the cotton as the time since application increased, and eight samples deposited more transferred material as the time since application increased. The visualization of these samples could be observed under white light as well when using an alternate light source.

Some similarities were seen in samples when analyzed using FTIR which allowed for the spectra to be separated into six different groups. Some of the samples displayed notably similar spectra to that of the unaltered skin which may suggest that the transferred material that was present on the cotton swatches was overwhelmed by the background material. No further discrimination or identification of the sunless self-tanning products could be made using this instrumental technique. There were several absorption peaks observed for each sample. The addition of material from the cotton swatch as well as the skin on which the sunless tanner was applied may have added another layer of intricacy
to the spectra. Regardless of effort made to subtract the spectra of the cotton and skin from the spectra of the transferred samples, peaks still proved difficult to assign to a given chemical component within the spectra of each product, thus making it nearly impossible to identify or individualize the products.

Analysis of the sunless self-tanners prepared directly from their packaging/bottles using GC-MS proved to be more useful in separating out the individual components of each product. Each commercial product displayed several peaks that were able to be identified when careful examination was applied to each chromatogram. Unique chemical ingredients were identified in each sample allowing for the discrimination of products, even among products of the same brand of sunless self-tanners. Most of these unique peaks were ingredients added either for fragrance or to help improve the products shelf life by providing antifungal/antimicrobial properties.

DHA was identified in fifteen of the sixteen samples. The one sample where DHA was not found was St. Tropez One Night Only Glow Body Lotion. It was expected that DHA would be absent from this product given that the intent of this product was to obtain a tanned look for a very short period of time and subsequently be able to wash the product off during the next shower. This product did display a peak for canthaxanthin, however. Canthaxanthin is a pigment added to both cosmetics and food in the United States and the United Kingdom.

GC-MS analysis of transferred material on white cotton swatches displayed peaks that were able to be matched to those seen in the chromatograms of the
sunless self-tanners prepared directly from the packaging or bottle. The peaks identified in the two transfer samples analyzed did not match any of the peaks that were earlier labeled unique to those products, but if a known sample is available for comparison, a stain containing transferred sunless self-tanner could be positively identified.

GC-MS proved useful as it was able to positively identify these products as a sunless self-tanner of a certain brand. It is understood that a stain on clothing produced by a sunless self-tanning product may not be the most probative piece of evidence in a forensic investigation, however, if the stains are analyzed, the detection and discrimination of the product could provide very valuable information to the investigation. Using both FTIR and GC-MS, an analyst could not only confidently say that the stain was produced from a transfer of sunless self-tanner onto the item of clothing, but also could discriminate between brands and identify the exact type of sunless self-tanner that is present if a known sample is available for comparison. This could be very useful in cases where limited physical evidence is present, especially those involving an altercation or violent act between individuals, including, but not limited to, sexual assaults, beatings, or homicides.

While transferred sunless self-tanners as pieces of evidence may seem insignificant when compared to bodily fluids or DNA evidence found at crime scenes, they should not be discredited or overlooked. These products are becoming more popular as the health risks associated with sun exposure are becoming more evident and their presence as evidence in crime laboratories is
likely to increase. It is important for analysts within a crime laboratory to understand how to analyze transferred self-tanners and to be able to identify them and provide probative information pertaining to an investigation.
6. FUTURE DIRECTIONS

This study showed that sunless self-tanners do in fact transfer onto clothing. This study was performed using white cotton swatches that showed a significant amount of contrast between the substrate and the transferred tanner. It would be beneficial to test whether sunless self-tanners transferred onto different fabric types and colors could be detected using the same methods. Analysis by GC-MS was done on only two samples containing transferred material. It would be beneficial to test whether the remaining transferred samples could be extracted and analyzed using GC-MS to produce similar results. Also, a blind study is suggested to see if an analyst could positively identify the brand and make of sunless self-tanners based on the results obtained from the instrumental analysis.

This study used sixteen different samples that could easily be obtained from drug or cosmetic stores. There are several hundred sunless self-tanners available to consumers, including more expensive products that are reported to provide more of a natural even tan, and spray tan booths within salons. It would be interesting to see if all products, produce similar results to those seen in this study when analyzed instrumentally,
APPENDIX A: IR SPECTRA OF TRANSFERRED SAMPLES

Figure 19. IR absorption spectrum of Sample 1: Olay Body Quench Touch of Sun applied once

Figure 20. IR absorption spectrum of Sample 1: Olay Body Quench Touch of Sun, applied over three consecutive days
Figure 21. IR absorption spectrum of Sample 2: L’Oreal Paris Sublime Bronze Luminous Bronzer

Figure 22. IR absorption spectrum of Sample 3: L’Oreal Paris Sublime Bronze Tinted Self-Tanning Lotion
Figure 23. IR absorption spectrum of Sample 4: Coppertone Gradual Tanning Lotion, applied once

Figure 24. IR absorption spectrum of Sample 4: Coppertone Gradual Tanning Lotion, applied for three consecutive days
Figure 25. IR absorption spectrum of Sample 5: CVS Sunless Tanning Lotion

Figure 26. IR absorption spectrum of Sample 6: Jergen’s Natural Glow 3 Days to Glow Lotion, applied once
Figure 27. IR absorption spectrum of Sample 6: Jergen’s Natural Glow 3 Days to Glow Lotion, applied for three consecutive days

Figure 28. IR absorption spectrum of Sample 7: Banana Boat Summer Color Lotion, applied once
Figure 29. IR absorption spectrum of Sample 7: Banana Boat Summer Color Lotion, applied for three consecutive days

Figure 30. IR absorption spectrum of Sample 8: Neutrogena Build-a-Tan Lotion, applied once
Figure 31. IR absorption spectrum of Sample 8: Neutrogena Build-a-Tan Lotion, applied for three consecutive days

Figure 32. IR absorption spectrum of Sample 9: Equate Beauty Self-Tanning Bronzing Spray
Figure 33. IR absorption spectrum of Sample 10: L’Oreal Paris Sublime Bronzing ProPerfect Misting Spray

Figure 34. IR absorption spectrum of Sample 11: Neutrogena MicroMist Self-Tanning Spray
Figure 35. IR absorption spectrum of Sample 12: Banana Boat Summer Color Self-Tanning Spray

Figure 36. IR absorption spectrum of Sample 13: Jergen's Natural Glow Daily Moisturizing Foam, applied once
Figure 37. IR absorption spectrum of Sample 13: Jergen’s Natural Glow Daily Moisturizing Foam, applied for three consecutive days

Figure 38. IR absorption spectrum of Sample 14: L’Oreal Paris Sublime Bronze Self-Tanning Towelettes
Figure 39. IR Spectrum of Sample 15: St. Tropez One Night Only Lotion

Figure 40. IR Spectrum of Sample 16: Vita Liberata Self-Tanning Foaming Mousse
LIST OF JOURNAL ABBREVIATIONS

Anal Bioanal Chem………………………… Analytical and Bioanalytical Chemistry
Anal Chim Acta……………………………… Analytica Chimica Acta
Aust N Z J Public Health…… Australian and New Zealand Journal of Public Health
Br J Dermatol……………………………… British Journal of Dermatology
Dermatol Clin…………………………… Dermatologic Clinics
Dermatol Ther…………………………… Dermatologic Therapy
Food Chem Toxicol ................................. Food and Chemical Toxicology
J Agric Food Chem .............................. Journal of Agricultural and Food Chemistry
J Invest Dermatol…………………….... Journal of Investigative Dermatology
JAMA........................................... Journal of the American Medical Association
Int J Cosmet Sci................................ International Journal of Cosmetic Science
Mikrobiyoloji Bül............................................. Mikrobiyoloji Bülteni
Nat Prod Commun.............................. Natural Product Communications
Z Für Lebensm-Un ters--Forsch ......................... Zeitschrift Für Lebensmittel-Untersuchung Und – Forschung
BIBLIOGRAPHY


34. Laureth-1 [Internet]. [cited 2014 Apr 27];Available from: http://www.cosmeticsinfo.org/ingredient/laureth-1


42. Keawsa-ard S, Liawruangrath B, Liawruangrath S, Teerawutgulrag A, Pyne SG. Chemical Constituents and Antioxidant and Biological Activities of the


CURRICULUM VITAE

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EDUCATION

Boston University School of Medicine, Boston MA
Masters of Science, Class of 2014
Major: Biomedical Forensic Sciences

St. Lawrence University, Canton, NY
Bachelor of Science, May 2012
Major: Biology
Dual Minor: Chemistry, African Studies
Study Abroad Program: Kenya, Fall 2010

RELEVANT EXPERIENCE

Boston University School of Medicine
May 2014

Lab Assistant, Bloodstain Pattern Analysis Course
- Responsible for the setup and cleanup of laboratory exercises
- Assisted instructor in demonstrations of each laboratory exercise
- Responsible for documenting materials used and ordering new materials when needed
- Assist students in the execution of each laboratory exercise and answer any questions

Boston Police Department, Crime Laboratory Unit
January 2014- May 2014

Internship
- Conducted thesis research in the Trace Evidence Section
- Observed the analysis of evidence
- Gained hands on experience within the lab and with relative casework
- Performed daily analysis of samples using Fourier transform infrared spectroscopy and Gas Chromatography-Mass Spectrometry
- Assisted criminalists when showing evidence to detectives and attorneys
- Attended webinars
RELEVANT EXPERIENCE CONTINUED

Wakuuzu, Friends of the Colobus Trust  
November 2011

Independent Work Study

• Classified thirty-eight primate skulls based on species, sex, and age, and examined sexual dimorphism and dentition of each
• Rehabilitated injured and sick primates by aiding in surgical procedures and responding to emergency calls
• Educated the public and local youth groups on the protection and migration patterns of primates in the area

RESEARCH EXPERIENCE

Boston Police Department, Crime Laboratory Unit, Boston, MA  
2013-2014

Thesis Research

• “The Detection and Discrimination of Sunless Self-Tanners Containing Dihydroxyacetone on Clothing Using Instrumental Techniques”

Saint Lawrence University, Canton, NY

Senior Year Research

• “Ceria Oxide Nanoparticle Effects on Rheumatoid Arthritis in Collagen Induced Arthritic Mice”

MEMBERSHIPS

Beta Beta Beta Biology Honorary Society  
2012- Present

American Chemical Society  
2008-2012

PROFESSIONAL CONFERENCES

American Academy of Forensic Sciences  
66th Annual Conference, Seattle, WA  
February 2014

SKILLS

Languages: Intermediate Spanish, Basic Swahili

General Forensic Laboratory Techniques: General crime scene documentation and photography, evidence collection and packaging, evidence sampling techniques and analysis, Fourier Infrared Spectroscopy Analysis with Attenuated Total Reflectance attachments (horizontal and diamond), Gas Chromatography-Mass Spectrometry
**TRAININGS AND CERTIFICATIONS**

- **Incident Command System Training (FEMA):** Level 1

  - **Forensic Technology Center for Excellence:** Webinar Training
    - “Collecting Footwear and Tire Impressions in Snow” - Jim Wolfe

**RELEVANT COURSEWORK**

- Molecular Biology of Forensic DNA Analysis
- Forensic Chemistry
- Forensic Biology
- Forensic Biology Laboratory
- Crime Scene Investigation
- Advance Crime Scene Investigation
- Medicolegal Death Investigation
- Forensic Pathology
- Criminal Law and Ethics I
- Criminal Law and Ethics II: Mock Court
- Trace Evidence Analysis
- Trace Evidence Analysis Laboratory
- Homicide Investigation
- Bloodstain Pattern Analysis
- Cellular Biology
- Genetics
- Human Anatomy
- Biochemistry
- Organic Chemistry
- Quantitative Chemical Analysis
- Multivariable Calculus
- Human Osteology