The Chemistry of Latent Prints from Children and Adults

Gary Mong, M.S.[1]
Steven Walter, Ph.D.[2]
Robert Ramotowski, M.S.[3]
Tony Cantu, Ph.D.[3]

Introduction

There are numerous literature sources that detail the composition of sweat. These studies typically used solvents or absorbent papers/materials to extract sweat samples directly from the skin surface of volunteers. However, these methods may extract different chemical compounds than those that would be deposited by brief contact with a surface (e.g., a latent print). In addition, the information contained in these studies deals with samples that are collected immediately after being excreted from the sweat gland. This is also not very representative of the fact that most examiners seldom recover fresh prints from the crime scene.

There was a need to not only study the chemical compounds present in a deposited latent print, but also examine how these compounds changed with time. The ultimate goal of obtaining this information was to guide future research efforts toward visualizing the more stable compounds (or even stable breakdown products) that are identified from this work. This would involve possibly developing new visualization methods or modifying existing techniques. Another aspect of this work involved the study of children's latent prints. Recent work done by Dr. Michelle Buchanan at the Oak Ridge National Laboratory (ORNL), in cooperation with Mr. Art Bohanan of the Knoxville, TN Police Department, found that children's prints are particularly difficult to recover from surfaces [1,2]. This was especially true in cases involving child abductions, when attempts to process car seats yielded little success beyond a few days for young children's prints.

Pacific Northwest National Laboratory (PNNL) was recently funded to continue and build upon ORNL's work. PNNL collected and analyzed samples from adults and children and then studied changes that occurred over time. The Savannah River Technical Center (SRTC) also conducted research in this area. The latter work focused on examining the breakdown products of lipid oxidation, and in particular, the formation of hydroperoxides.

Work Performed by the Pacific Northwest National Laboratory

The group at PNNL collected and analyzed samples from approximately eighty-five subjects ranging in age from a young child to a middle-aged adult. The preliminary results indicate that not only do young children leave considerably less residue on a surface (in some cases as little as 1/20 that of adults), the lipid portion of their prints is composed primarily of cholesterol, cholesterol esters, and fatty acids. Most of these compounds breakdown relatively rapidly, except for the saturated fatty acids (e.g., stearic, palmitic). Unfortunately, these saturated compounds are not very chemically reactive.

Latent prints were collected from volunteers by having them place sebaceous prints on GFA glass fiber filter papers (Van Waters and Rogers, 4.25 cm circles). With adult samples, extractions were done soon after deposition (as reasonable as possible), and then after 10, 30 and 60 days. With children's prints, extractions

[1] Pacific Northwest National Laboratory, Richland, WA.
[2] Savannah River Technical Center, Aiken, SC.
[3] United States Secret Service, Forensic Services Division, Washington, DC.

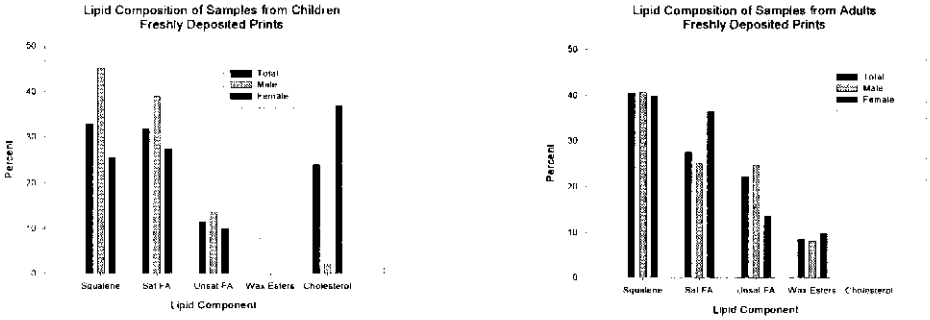

Figure 1: The lipid composition (by weight percent) of prints deposited by children (left) and from adults (right).

were done only after deposition and then after 30 days. The extraction solvent was chloroform. Samples were derivitized using diazomethane.

Figure 1 shows a comparison of recently deposited latent prints from 10 adults and 8 children (aged 10-12). The most noticeable differences occur with wax esters and cholesterol. The anomaly that occurs with the cholesterol peak with children was caused by a group of four females whose prints contained approximately 85-90% cholesterol. Due to limitations placed on the use of human subjects as volunteers for this study, the individuals could not be re-sampled to verify the observed results. Although children have significantly more cholesterol than adults, the average amounts are typically less than ten percent. PNNL is in the process of preparing their final report, which will contain detailed information relating to the aging studies.

PNNL also performed a squalene aging study. They found that approximately 40% of the squalene residue had been converted to other materials within a twenty-day period. Chromatographic peaks were observed before and after the parent squalene peak, indicating that products of lower and higher molecular weight were being formed. A similar test was performed with oleic acid. After approximately seventeen days, the oleic acid peak was virtually gone. The two primary breakdown products were found to be nonanedioic acid and 9-epoxy oleic acid.

Work Performed by the Savannah River Technical Center (SRTC)

The experiments being done at the SRTC involved directly analyzing compounds present in a latent print (e.g., squalene) and characterizing their breakdown products. A series of standard lipids representative of the various lipid classes found in latent prints were used. These compounds included triglycerides, fatty acids, wax esters, cholesterol, cholesterol esters, and a sensitizer (protoporphyrin IX dimethyl ester, 0.01% of the overall mixture). The sensitizer was added to catalyze the reaction between triplet oxygen and light to form singlet oxygen (a highly reactive species). A 100 μg amount of this mixture was placed onto a glass slide and aged in various conditions (e.g., light/no light, and/or indoors/outdoors).

The oxidation of unsaturated lipids is accelerated by metals, light, heat, and by several initiators and can operate through autoxidation or photo-oxidation pathways [3]. The primary autoxidation products are allylic hydroperoxides. The double bonds present in unsaturated compounds typically remain, but may change position and/or configuration. Hydroperoxides may also undergo further changes. In some cases, volatile compounds of lower molecular weight are formed (e.g., aldehydes) which often cause the familiar odors associated with lipid breakdown. However, this is not the dominant process. For example, the thermal decomposition of linoleate hydroperoxide at 210°C gives 82% of the dimer product and only 4-5% volatile organic compounds. Another possibility involves the formation of rearrangement products (with the same chain length) and products of further oxidation or of reaction with solvent (or other compounds present). The final pathway involves the formation of products of higher molecular weight (e.g., dimers, polymers). Photo-oxygenation involves

interaction between a double bond and the highly reactive species singlet oxygen (produced from ordinary triplet oxygen by light in the presence of sensitizers, like chlorophyll, erythrosine, rose bengal, methylene blue, etc.).

The SRTC proposed measuring the amount of hydroperoxides present by chemiluminescence. Chemiluminescence is produced by the reaction of hydroperoxides and luminol in the presence of cytochrome c. Luminescence levels will be measured by adapting a published chemiluminescence assay (using an integrating CCD camera) [4].

The SRTC (like PNNL) found that unsaturated compounds are depleted rapidly from a latent print deposit, even in cool, dark storage conditions. Oxidation, not evaporation, was the primary reason that these unsaturated compounds were not detected. Some loss of saturated fatty acids was observed. Samples on glass slides that were subjected to outdoor conditions (e.g., rain) lost most of the lipids in the mixtures (with the exception of wax esters). Aged lipid samples (approximately five months) formed some polymeric material that adhered to the slides. Unlike the original mixture, this material was not soluble in warm diethyl ether.

Squalene appears to be the most reactive of the lipids. Squalene exposed to air will begin to oxidize relatively quickly and eventually form a waxy solid. One experiment indicated that 98% of a thin film of squalene was lost after a four hour exposure to sunlight (a similar loss required four days of exposure to normal room lighting conditions). An experiment done in which the UV component of sunlight was filtered from the squalene resulted in 57% of the deposit surviving four hours of exposure. Squalene oxidized with ultraviolet radiation (and thus forming $^1O_2$) is known to form volatile compounds like acetaldehyde, formaldehyde, acetone, malonaldehyde, and 6-methyl-5-hepten-2-one [5]. As with other lipids, oxidation is the primary mechanism responsible for squalene's disappearance. When a nitrogen atmosphere is used, 65% of squalene remained after a four hour exposure to sunlight.

Using another recently published chemiluminesce assay method [6], the SRTC was able to quantify the amount of hydroperoxides present in a sample of squalene that had been exposed to a month of direct sunlight. The sample was found to have about 0.07 moles of hydroperoxide per mole of squalene. Subsequent testing indicates that the hydroperoxide concentration peaks within about two days after exposure to direct sunlight. Another experiment found that after one month of exposure, 10% of the squalene residue was composed of hydroperoxides. In future experiments, additional lipids will be analyzed as well as sebum from latent prints.

Conclusion

The SRTC data has helped to better understand some of the results observed in the PNNL experiments. The results obtained from both projects will provide a better understanding of latent print chemistry involving both children and adults. In addition, it is hoped that the aging study data will help direct future research efforts by identifying stable compounds that may eventually be visualized physically, chemically, or optically.

References

[1] Bohanan, A. "Latents from Pre-pubescent Children Versus Latents from Adults," *Journal of Forensic Identification*, V. 48, No. 5, 1998, pp. 570-573.

[2] Buchanan, M.V.; Asano, K.; and Bohanan, A. "Chemical Characterization of Fingerprints from Adults and Children," *SPIE Proceedings: Forensic Evidence Analysis and Crime Scene Investigation*, V. 2941, 1996, pp. 89-95.

[3] Gunstone, F.D. *Fatty Acid and Lipid Chemistry*. Chapman & Hall: London, 1996.

[4] Miyazawa, T.; Fujimoto, K.; and Kaneda, T. "Detection of Picomole Levels in Lipid Hydroperoxides by a Chemiluminescence Assay," *Agric. Biol. Chem.*, V. 51, 1987, p. 2569.

[5] Yeo, H.C.H. and Shibamoto, T. "Formation of Formaldehyde and Molonaldehyde by Photo-oxidation of Squalene," *Lipids*, V. 27, No. 1, 1992, p. 50.

[6] Pinchuk, I.; Schnitzer, E.; and Lichtenberg, D. "Kinetic Analysis of Copper-induced Peroxidation of LDL," *Biochimica et Biophysica Acta*, V. 1389, No. 2, 1998, pp. 155-172.