Chemical characterization of fingerprints from adults and children

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ABSTRACT

The observation that the fingerprints of children disappear from surfaces more quickly than those of adults initiated a study to characterize the chemical components in fingerprints. Samples were obtained from about 50 individuals ranging in age from three to 64 by extracting chemicals from the fingertips using rubbing alcohol. Using combined gas chromatography/mass spectrometry, a wide range of compounds were identified. It was found that the chemical compositions of fingerprints were quite different in children and adults. In general, the samples obtained from children contained higher levels of relatively volatile free fatty acids. Samples from adults were found to have higher concentrations of less volatile long chain esters of fatty acids. These esters are thought to originate from sebaceous glands located on the face and the levels of these compounds increase substantially after puberty. In addition to these compounds, a variety of other compounds were observed that could be used to develop improved methods for fingerprint detection at a crime scene. Further, the observation of specific compounds raises the possibility of being able to identify personal traits (gender, habits, diseases, etc.) via the analysis of components in fingerprints and/or skin.

Keywords: fingerprints, chemical analysis, gas chromatography/mass spectrometry

1. INTRODUCTION

In July 1993, a three-year-old girl was abducted and brutally murdered in Knoxville, TN. The suspect initially confessed, but later recanted his confession. This made it imperative that evidence linking the child to the suspect be found. Despite witnesses placing the child in the suspect's vehicle, a thorough examination of the vehicle did not yield any fingerprints from the child; only the suspect's fingerprints were found. This same phenomenon was observed previously in a child kidnaping where the vehicle could not be examined for prints until four days after the crime.

This raised the possibility that the fingerprints from children did not last as long on surfaces as fingerprints from adults. After contacting fingerprint experts from several agencies in this country and abroad, no information about the disappearance of children's fingerprints from surfaces could be found. To test out this possibility, a simple experiment was conducted. In August 1993, children were asked to deposit fingerprints on the inside of a number of vehicles. Within 24 hours, no fingerprints could be found. As a follow-up, a group of children and adults were asked to touch the outside surfaces of new, clean plastic and glass soda bottles, which were placed in cases. Half of the cases were stored in a basement at relatively constant temperature and humidity levels. The other half were placed in the back of an automobile, which was subjected to a range of temperatures, including summer temperatures of greater than 85°F. Samples were tested by conventional dusting over a several day period. It was discovered that the children's fingerprints disappeared within 24 hours, while the prints from adults lasted at least several days. Further, the fingerprints from bottles in the basement lasted much longer than the ones in the cars. These samples were collected every 30 days for the entire year of 1994 and similar results were observed each time. The only difference observed was that the children's fingerprints disappeared faster at higher temperatures.

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The relationship between the disappearance of the fingerprints and temperature suggested that there was a difference in the chemical composition of fingerprints between adults and children. Literature searches showed very little information on the chemical composition of fingerprints and nothing on the fingerprints of children. A study was therefore initiated to analyze the components in the fingerprints of children and adults to ascertain if an explanation for the faster disappearance of children's fingerprints could be obtained.

2. EXPERIMENTAL

2.1 Sample preparation

Volunteers ranging in age from three to 64 were asked to submit samples. The sampling protocols were reviewed and approved by the Oak Ridge National Laboratory/Oak Ridge Associated Universities (ORNL/ORAU) Committee for Human Studies prior to initiating this study. Approximately 1 mL of rubbing alcohol (70% isopropanol in water) was placed in a small (4 mL) sample vial sealed with a Teflon-lined screw closure. The vials were cleaned prior to use by sonicating in acetone for 10 minutes and dried at 100°C for a minimum of one hour. To obtain a sample, the subject placed a fingertip on top of the vial and shook the rubbing alcohol against the fingertip for one minute. In some instances, the subject was asked to wipe the tips of the fingers across his/her forehead prior to shaking the sample vial against the fingertip. The vials were labeled by a code number to protect the identity of the subject. Prior to analysis, the samples were concentrated under a small stream of argon gas until approximately 50 to 100 μL of solution remained. Some samples were analyzed directly at this stage. Others were derivatized using a methylating reagent to allow polar compounds to be analyzed more readily. In this case, 100μL of Methyl-8® reagent (Pierce Chemical Company, Rockford, IL) was added to the concentrated sample solution. The vial was then heated for 20 minutes at 60°C and the sample was then ready for analysis.

2.2 Sample Analysis

The samples were analyzed on a combined gas chromatograph/mass spectrometer consisting of a Varian 3400 gas chromatograph interfaced to a Finnigan ITS40 quadrupole ion trap mass spectrometer. A fused silica capillary column, 30 m in length and 0.25 mm ID with a bonded (5%-phenyl)methylpolysiloxane stationary phase (DB-5, J&W Scientific, Folsum, CA) was used to separate the components prior to analysis in the mass spectrometer. Helium was used as the carrier gas at a head pressure of 5 psi. The injector temperature was held at 280°C and the column oven was temperature programmed, starting at 100°C for one minute and ramping at 5°C/min to 280°C, where the column was held up to 30 minutes. The mass spectrometer transfer line was maintained at 280°C and the manifold heater for the analyzer cell was maintained at 220°C. All mass spectra were obtained using electron ionization (70 eV). In some cases, chemical ionization spectra were obtained using isobutane or methane as a reagent gas to verify molecular weights of the observed compounds. In this case a Hewlett-Packard 5985 GC/MS, equipped with a similar chromatographic column and operated under similar chromatographic conditions, was employed. The reagent gas was introduced into the ion source at approximately 0.5 torr and the chemical ionization plasma was formed using 200 eV electrons.

3. RESULTS AND DISCUSSION

During the course of these studies, nearly fifty subjects were studied, with about half ranging in age from three to 13 years and the other half, from 15 to 64 years. The chromatographic profiles obtained from the samples clearly fell into two classes, one made up of prepubescent children and the other from adults. The total ion chromatogram shown in Figure 1 is taken from a four year old boy and is typical of the profiles obtained from children. The early eluting peaks are composed primarily from long chain carboxylic acids having from twelve (C_{12}) to more than twenty-six (C_{26}) carbons, including palmitic and stearic acids. Because the samples were methylated, these compounds were detected as methyl esters of the acids. These compounds clearly are the major components in the samples obtained from children. Figure 2 is a total ion chromatogram obtained from an adult male (age 27). This chromatogram is quite distinct from the one in Figure 1 and is quite typical of those obtained from adults. In this profile, long chain carboxylic acids are also observed, but at a much lower level than in the samples from children. However, a number of higher molecular weight compounds are also observed at retention times greater than 50 minutes. These compounds, which are not observed in the child's profile in Figure 1, are long chain alkyl esters of carboxylic acids, such as C_{16} esters of C_{18} acids. General structures of the long chain carboxylic acids and esters are given in Figure 3.

Samples taken after the subject had wiped his/her forehead revealed even larger amounts of the long chain alkyl esters. These esters are members of a class of compounds called lipids. Most of the lipids on skin are thought to originate from sebaceous glands[1] and the highest density of these glands occur on the scalp and face, with none on the palms. Because an individual frequently touches his face and hair, it is logical that this material is transferred to the fingertips and can be found in fingerprints. Further, in adults, it is thought that over 95% of the skin surface lipids arise from sebaceous excretions.[2] The surface lipids in children, on the other hand, are thought to arise from the

epidermis and are present at far lower levels than adults, with sebaceous excretions increasing only after puberty. This difference in the content of these lipids may account for the observed differences in the disappearance of latent fingerprints from surfaces. At elevated temperatures, the lower molecular weight, volatile carboxylic acids that are prevalent in young children would tend to evaporate from the surface. With only low levels of the higher molecular weight, less volatile long chain esters, it is quite likely that little material would remain from a child's fingerprint to allow the print to be observed using conventional dusting techniques. Conversely, the higher levels of the alkyl esters found in adult fingerprints would remain on the surface longer, allowing fingerprints to be observed over longer periods of time.

Squalene (see Figure 3) was by far the most abundant compound identified in the extracts, even though the solubility of this compound in alcohol is relatively low. This compound is an intermediate in the biosynthesis of cholesterol[3] and is seen at a retention time of approximately 38 minutes in the chromatograms shown in Figures 1 and 2. Note that the levels of squalene are typically lower in children than adults, which again is probably a reflection of the fact that this compound originates primarily from sebaceous glands.[2] Cholesterol was observed in all samples studied and may be seen at a retention time of approximately 45 minutes in the chromatograms in Figures 1 and 2. This compound is thought to arise primarily from the epidermis[2] and is typically observed at much higher levels in children than in adults. The chromatogram in Figure 2 was from an adult that had unusually high response for cholesterol compared with the other adults tested. For the other adult samples, the cholesterol peak was present, but in much lower quantities than a related compound, cholesteryl acetate. Many structural isomers of this compound exist, and one is shown in Figure 3. This compound can be observed in the chromatographic profile shown in Figure 1, which is the sample obtained from the child. The levels of cholesterol and cholesterol acetate isomers were observed to change between different individuals. This again may be observed in Figure 2, where this adult male had a large cholesterol peak and little cholesteryl acetate.

Other compounds were also identified in the samples taken from the fingertip extracts. Samples taken from the fingertips of smokers contained traces of nicotine. This compound may have originated from handling tobacco products or from exposure to tobacco smoke, rather than from excretion of the compound from the skin. However, during these studies nicotine was also identified in the fingertip extract of an adult who had quit smoking cigarettes two weeks prior to the experiment, but was chewing nicotine gum. In a few samples, traces of steroids were also observed in fingertip extracts. The presence of steroid hormones and their metabolites has been reported[2] in human skin and has been related to gender and different physiological conditions, including diet, cancer, and others.

The results of this study have shown that there is indeed a difference in the composition of materials present in the fingerprints of children and adults. The lower levels of higher molecular weight, less volatile materials in children's fingerprints could explain the disappearance of fingerprints from crime scenes. As a result, for any crime involving a child, it is imperative that fingerprints be examined as soon as possible. A systematic study of the rate of disappearance of specific fingerprint components as a function of temperature and other environmental parameters is planned to assess which compounds are retained on surfaces. These studies will be used to identify specific components found in the fingerprints of both children and adults that could be used for the development of an optical detection method that would allow fingerprints to be detected more reliably.

The general chemical characterization of components in fingerprints in our laboratory is continuing. In these initial studies, rubbing alcohol was used to extract components directly from the fingertips. This permitted more material to be collected for analysis than simply extracting individual prints off a non-porous surface. Rubbing alcohol was chosen as a solvent in this study due to its relatively low toxicity. However, it should be noted that this solvent will not extract all the compounds present on the surface of fingertips, and the compounds found in this study are primarily those that have appreciable solubility in this solvent. Other solvents and/or sampling methods are being investigated to allow a wider variety of components to be identified as part of these studies.

In another area of research, we are investigating potential uses of the chemical composition of fingerprints in forensic, clinical, and other applications. The fact that the types and quantities of some compounds change from person to person opens the possibility that one might be able to analyze components in fingerprints and/or extracts taken from fingertips and obtain information about the individual. For example, by analysis of fingerprints, narrowing down the list of potential suspects may be possible based on the presence or absence of targeted components, such as hormones, nicotine, illegal drugs, and others. Excretion of amphetamines in human sweat has been documented.[4] Thus, the potential exists for non-invasively collecting samples and detecting drugs and/or drug metabolites in materials obtained from fingerprints and/or skin. This would eliminate the need to collect and handle potentially hazardous biological samples, such as blood and urine. Further, with development of sensitive analytical schemes based on mass spectrometry, optical, or other methods, screening individuals rapidly for the presence of illegal drugs may be possible, rather than sending the samples to a remote laboratory for analysis and waiting days or even weeks for results. For example, we have shown the ability to detect trace levels of drugs in microliter quantities of milk using quadrupole ion trap mass spectrometry.[5] This technique minimizes the need for sample preparation and can be completed in a few minutes rather than four or more hours by conventional gas chromatography/mass spectrometry. The ability to detect

targeted components rapidly in fingerprints and/or skin would have broad application in forensic investigations, law enforcement activities, and clinical applications.

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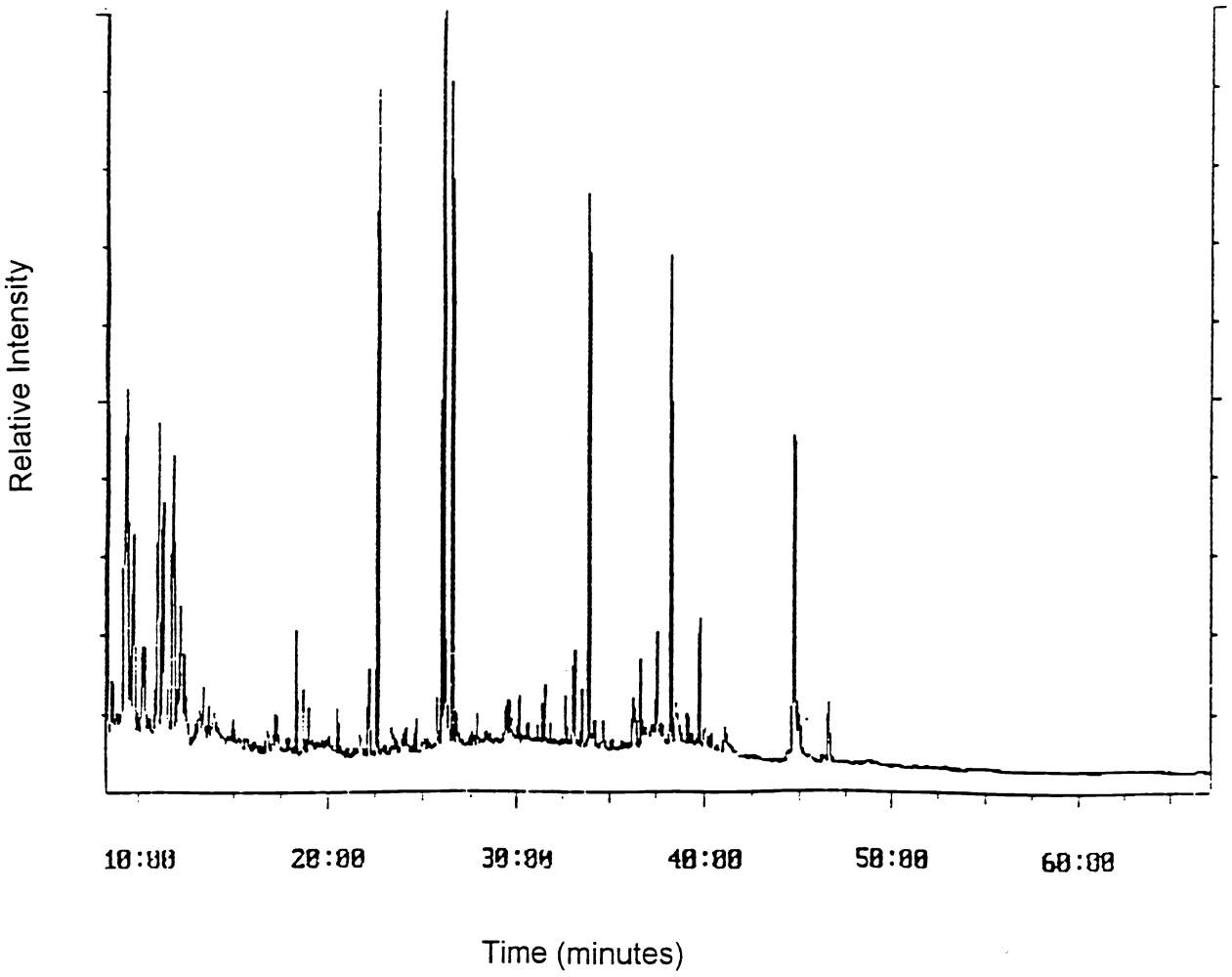

Figure 1. Total ion chromatographic profile of fingertip extract from four year old male. Peaks at approximately 38, 45 and 47 minutes are squalene, cholesterol, and an isomer of cholesteryl acetate, respectively.

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