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Characterizing and classifying water-based lubricants using direct analysis in real time®–time of flight mass spectrometry

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ABSTRACT

Lubricant analysis is a relatively recent addition to the examination protocol in sexual assault cases by the forensic science community. Currently, lubricants cannot be unequivocally identified, although their presence can be determined based on the detection of a few chemical components, i.e. polydimethylsiloxane, polyethylene glycol, glycerol or nonoxynol-9. Confirmation of their presence typically requires that an authentic reference sample be submitted and compared to the unknown sample to determine if they potentially came from the same source. In this study, 33 individual personal water-based lubricants were characterized by direct analysis in real time–time of flight mass spectroscopy (DART–TOFMS). The resultant mass spectral data were evaluated using well-established multivariate statistical techniques, such as principal component and linear discriminant analysis. Statistical analysis revealed six different groupings within the data that could be correlated to sub-categories of water-based lubricants that contain additives in the form of anesthetics, sensation enhancers and flavorings. This variability in the personal lubricant sources can be utilized to aid in identifying the specific type of lubricant when only a questioned sample is available.

1. Introduction

Sexual assaults are an unfortunate reality in modern society, with a recent survey conducted by the National Center for Injury Prevention and Control revealing that roughly 1 in 5 women and approximately 1 in 71 men will encounter a sexual assault in their lifetime [1]. Even though this statistic alone is concerning, condom usage has also drastically increased in sexual assaults over recent years, as sexual assailants have consciously attempted to mitigate the transfer of biological evidence. A study revealed that prevalence rates of condom usage in sexual assaults can range anywhere from 11 to 16%, based upon a large sample size of sexual assault cases from select cities of the U.S [2]. Consequently, in instances where sexual assaults have involved the use of a condom, increased emphasis must be placed on the characterization of lubricant evidence in order to provide an evidential link between the suspect and the victim or the suspect and the crime scene.

In comparison to other trace evidence disciplines, the forensic analysis of lubricants is a relatively new concept in sexual assault investigations. Sexual lubricants are typically classified into two main categories; condom and bottled personal lubricants. There is a lack of studies in the open literature examining the significance of lubricant evidence in instances of sexual assaults and within this group of literature, the focus is primarily on condom lubricants rather than bottled personal lubricants. There are four main types of bottled lubricants currently on the market including: water-based, silicone-based, oil or petroleum-based and edible/organic. Within these types of lubricants there are unique compounds that differentiate them from the other types and thus they should be beneficial in indicating a specific lubricant class (Table 1). Outside of these groupings, some lubricant samples can include additives designed to impart a specific functionality or purpose. For instance, lubricants can contain anesthetics (e.g. lidocaine or benzocaine) which act as numbing agents or anal desensitizers. Others may contain flavoring agents (e.g. maltol, ethyl maltol) which provide an aroma and/or flavor to the lubricant, while some may contain compounds like menthol and capsaicin which afford a change of sensation, (i.e. cooling or warming, respectively). Currently, identifying these components in an effort to characterize sexual lubricants has not been addressed by the research community.

Previous research has focused on identifying the major component in the lubricant sample, e.g. polydimethylsiloxane (PDMS), poly(ethylene glycol) (PEG), glycerol, or nonoxynol-9.

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Table 1
Common chemical components identified in personal sexual lubricants.

Lubricant group	Component/s
Water	Glycerol, poly(ethylene glycol), methyl/propyl paraben, water, carboxymethyl cellulose, propylene glycol
Silicone	Poly(dimethylsiloxane), hydroxyl-terminated poly(dimethylsiloxane), cyclomethicone, cyclopentasiloxane
Oil/petroleum	Mineral oil, paraffin, stearic acid, cetyl alcohol, lanolin
Organic/edible	Glucose, chlorhexidine, methyl/propyl paraben, aloe vera gel, coconut/almond/olive oil, coconut/shea butter

Current techniques including gas chromatography–mass spectrometry (GC–MS) [3–6], pyrolysis gas chromatography–mass spectrometry (Py-GC–MS) [3,4,7], Fourier transform infrared spectroscopy (FTIR) [4,8], and microscopy [8,9], will identify the major components. However, due to the significant concentration of these major lubricants, it is difficult to isolate and identify the minor components that can provide more discriminating information, using these traditional techniques.

Direct analysis in real time–time of flight mass spectrometry (DART–TOFMS) is an ambient ionization technique that is capable of rapidly analyzing samples in any state with high resolution and accurate mass detection, while requiring little to no sample preparation. Although it is still a relatively novel technique, DART–TOFMS has been used to characterize a wide variety of trace evidence including; drugs [10–17], inks [18–20], chemical warfare agents [21], and explosives [22,23] primarily due to the rapid and accurate spectrometric analysis that it provides. DART–TOFMS was recently recognized as a viable technique in the analysis of evidence from sexual assault cases [24]. A study by Musah et al. demonstrated that DART–TOFMS was capable of detecting condom lubricant components, such as the spermicide nonoxynol-9, left by fingerprints on condom wrappers. The authors concluded that this technique required significantly less sample and was thus was less destructive than traditional mass spectrometric techniques (e.g. GC–MS, LC–MS) [24]. Furthermore, lubricant analysis using conventional chromatographic techniques suffers from a significantly longer analysis time than DART–TOFMS, due principally to the amount of sample preparation required and the time necessary to chromatographically separate the components in the lubricant mixture. Additionally, baseline resolution of these lubricant mixtures can be difficult to attain depending on the type of lubricant base used, such as a silicone or oil [6]. Separation issues are insignificant in DART–TOFMS analysis, where molecular ions of every component in the sample enter directly into the TOF mass spectrometer, which provides the necessary separation of compounds within seconds. Therefore, each peak is representative of an individual compound and since the TOF mass spectrometer provides high resolution, each peak is baseline resolved.

With the benefits of using DART–TOFMS to analyze lubricant samples, the aim of this study was to develop an analytical protocol to characterize personal lubricants. By characterizing these samples and identifying chemical sub-groupings, it will be feasible to use this information to characterize unknown lubricant samples collected in sexual assault kits. This would provide a more specific determination of the type of lubricant used in the commission of a crime, instead of just being able to identify the main lubricant base, such as PDMS, PEG or glycerol. It could also be used in a classification scheme for unknown sample analysis of personal lubricants and eventually condoms, similar to the American Standard for Testing & Materials standard method E1618 that is used to classify unknown ignitable liquids samples [25].

2. Materials and methods

2.1. Materials

For this study, 33 personal water-based lubricants (refer to Table 2) were purchased in-store and via the online vendors eBay and Amazon. Research grade helium and nitrogen gas cylinders were purchased through Air Liquide (Houston, TX, USA). Glycerol, maltol, ethyl maltol, triethyl citrate, menthol, and triethanolamine standards and capillary tubes were purchased from Fisher Scientific (Pittsburgh, PA, USA). Benzocaine, propylene glycol, methyl paraben, propyl paraben, Fomblin®-Y and PEG with an average molecular weight of 600 (PEG600) standards were obtained from Sigma–Aldrich (St. Louis, MO, USA).

2.2. Sample acquisition parameters for AccuTOF-DART

Positive and negative-ion mass spectra were acquired using a JEOL (Toyko, Japan) AccuTOF™ mass spectrometer (JMS-4000LC) coupled with an IonSense (Peabody, MA) DART® ionization source. The DART ion source was operated using helium as the ionizing gas at a flow rate of approximately 3.6 L/min; the gas temperature was maintained at 350 °C. The needle electrode potential was held at 2 kV and an exit grid voltage of 250 V was used for the positive-ion mode. The factory recommended orifice 1, orifice 2 and ring lens voltages of 20, 5 and 5 V, respectively were utilized, as this minimized the fragmentation of the analyte ions, thus aiding in data interpretation. The peaks voltage (Rf ion guide voltage) was set to 600 V to allow detection of ions greater than a mass-to-charge ratio (m/z) of 60. This value was selected as it eliminated the largest interference background ions such as protonated water, protonated water dimer and ammonium ion, while ensuring adequate sensitivity of the m/z of the analytes of interest. Mass spectra were acquired using JEOL Mass Center over the mass range of m/z 60 to 1000 at a sampling and recording interval of 0.25 ns and 1 s, respectively. The microchannel plate (MCP) detector voltage was maintained at 2100 V for the duration of the analysis.

Personal lubricants were sampled without any preparation, by dipping the closed end of a capillary tube into the sample and positioning the sample between the DART ion source and the MS inlet (i.e. sample gap). The DART ion source was positioned approximately 1 cm from the inlet of the detector. The sample-coated capillary tube was placed roughly 1 mm from the ceramic cap of the DART ion source and waved for a period of 5 s in front of

Table 2
List and the number of water-based lubricants used in the study and the classifications.

Sample name	Lubricant marketing type
Adam & Eve (1)	Water-based
Anal Eze (3)	Anesthetic (benzocaine)
Astroglide Liquid (1)	Water-based
ID Glide (1)	Water-based
Jo H_2O Cooling (3)	Sensation (cooling)
Jo H_2O Warming (1)	Sensation (warming)
Jo H_2O Water (1)	Water-based
KY Jelly Personal Lubricant (1)	Water-based
KY Ultragel (3)	Water-based
Passion Anal Desensitizing Lubricant (2)	Anesthetic (lidocaine)
Sasmar Warming (3)	Sensation (warming)
Slippery Stuff (3)	Water-based
Wet Flavored Blueberry (2)	Flavored water-based
Wet Flavored Kiwi Strawberry (1)	Flavored water-based
Wet Flavored Passionate Fruit Punch (1)	Flavored water-based
Wet Flavored Raspberry Pomegranate (2)	Flavored water-based
Wet Flavored Sweet Cherry (1)	Flavored water-based
Wet Flavored Watermelon (1)	Flavored water-based
Wet Nuru (1)	Water-based