J Forensic Sci, May 2007, Vol. 52, No. 3
doi:10.1111/j.1556-4029.2007.00411.x
Available online at: www.blackwell-synergy.com

Gareth P. Campbell,[1] *M.Sc.(Hons) and Amanda L. Gordon,*[2] *M.Sc.(Hons)*

Analysis of Condom Lubricants for Forensic Casework*

ABSTRACT: The detection of DNA is inhibited in cases of sexual assault involving condom use. Trace evidence, including condom lubricant residues, provides crucial associative evidence in such cases. The existing Fourier transform infrared spectroscopy (FTIR) methods for lubricant analysis and detection are limited with regard to sensitivity and discrimination. The aim of this research was to establish a new method as an alternative to FTIR for the analysis of condom lubricant residues. Pyrolysis gas chromatography-mass spectrometry (PyGC-MS) and GC-MS are highly sensitive methods of analysis for a wide range of chemical substances. PyGC-MS and GC-MS were used to analyze condom lubricants in standard solution, from clean swabs and from postcoital swabs. Pyrolysis of polydimethylsiloxane (PDMS) lubricant forms cyclic products known as cyclic dimethyl siloxanes (DMS), which are separated and detected by the GC-MS. The polyethylene glycol (PEG) lubricant can be analyzed by GC-MS directly from solution. The methods of extraction and analysis presented in this paper were shown to be significantly more sensitive than FTIR for the analysis of PDMS and PEG condom lubricants. PDMS was detected as low as 1 μg in standard solution and from clean swabs using the PyGC-MS method. PEG was detected as low as 0.5 μg from standard solution and 50 μg from clean swabs using the GC-MS method. Unfortunately, we were unable to provide further discrimination between condom brands and subbrands. The methods established throughout the research were used successfully to detect condom lubricants from donated postcoital swabs. Lubricants were detected in abundance on swabs 12 h postcoitus. Recommendations are made regarding implementation of new methods for routine analysis of casework samples along with strict pyrolysis interpretation criteria to minimize the possibility of misinterpretation of false positives.

KEYWORDS: forensic science, condom, lubricant, polydimethylsiloxane, polyethylene glycol, pyrolysis, gas chromatography-mass spectrometry

The term "condom lubricant" can be defined as a slippery substance, applied to condoms during the manufacturing process, to facilitate penetration. Condom lubricants are readily transferred from one individual to another through protected intercourse. Subsequent detection of lubricant residue provides important associative evidence in sexual assault cases where DNA is not recovered.

In the past decade there, has been an increase in sexual assault cases involving condom use (P. Thompson, personal communication). The possible reasons for this are that offenders may want to block the transfer of seminal fluid because they know of the use of DNA evidence in the justice system; they may be repeat offenders and have their DNA profile stored on a national database; or they may be abusing a person known to them and may use a condom for contraceptive purposes. It is also possible that offenders may use a condom as a barrier to sexually transmitted infections (STIs).

The majority of condoms on the market are made from natural latex rubber. However, there are products available made from alternative materials including polyurethane (e.g., Durex Avanti) and natural materials (e.g., sheep caecum used in the Trojan Naturalamb condom) (1). Chemical treatments give rise to the desired properties of the latex and condoms are dusted with particulates to prevent self-adhesion and increase lubrication properties (P. Thompson, personal communication). The final stage of manufacture, in all but a few cases, involves the application of a lubricant. The lubricant formulation may contain a spermicide (e.g., nonoxynol-9), flavors, coloring, or fragrances (2). The majority of condoms available on the New Zealand market contain either a silicone-based lubricant in the form of a low-molecular-weight silicone oil, polydimethylsiloxane (PDMS), or a water-soluble condom lubricant, polyethylene glycol (PEG).

PDMS (Fig. 1) contains a mixture of oligomers ranging in molecular weight up to at least 20,000 amu. PDMS formulations are used in many industries including cosmetics and pharmaceuticals (3). PDMS used for condom lubrication is a colorless, odorless liquid with an average viscosity of around 200 cSt, although this may vary between manufacturers (4). For example, Gold Knight condoms are lubricated with PDMS that has an average viscosity of 350 cSt (J. Bell, personal communication). PDMS is a common condom lubricant because it possesses favorable properties: PDMS is not absorbed into the latex sheath, ensuring the integrity of the condom; it is not absorbed into the body; and it has good lubrication properties (P. Thompson, personal communication). Therefore, PDMS will persist on skin and mucous membranes for an extensive time period, allowing subsequent forensic detection.

PEG (Fig. 2) is present on condoms in a low-molecular-weight form (e.g., PEG300 or PEG400); it is a clear viscous liquid and is often used in combination with a spermicide (1).

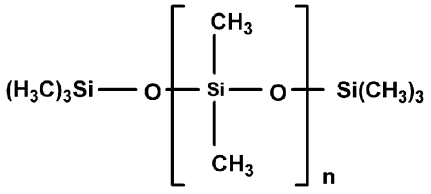

FIG. 1—*Polydimethylsiloxane (2).*

[1]The Department of Chemistry, The University of Auckland, Private Bag 92019, Auckland, New Zealand.
[2]The Institute of Environmental Science and Research Ltd., Private Bag 92021, Auckland, New Zealand.

*Presented orally at The 16th International Symposium of Analytical and Applied Pyrolysis, Alacante, Spain, May 23–27, 2004.

Received 6 Feb. 2006; and in revised form 1 Oct. 2006; accepted 29 Oct. 2006; published 5 April 2007.

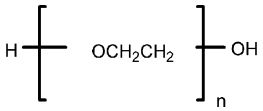

FIG. 2—*Polyethylene glycol (2).*

Several methods have previously been described for the detection of PDMS condom lubricants. Fourier transform infrared spectroscopy (FTIR) is a commonly used technique to detect PDMS in casework. It is a quick, simple, and cost-effective technique that provides a good degree of sensitivity. FTIR provides a good screening technique for PDMS, although discrimination between PDMS-based condom lubricant samples is not possible (A. Kearns, personal communication).

Other methods that have been applied to PDMS analysis include desorption chemical ionization-mass spectrometry (DCI-MS) (5), numerous gel permeation chromatography (GPC) methods (5,6), and more recently, Raman spectroscopy (7) and capillary electrophoresis (8). Although there are a number of methods for PDMS analysis, the majority of them have limited application in casework due, primarily, to instrument availability. FTIR is currently the primary analytical technique used in forensic laboratories for lubricant analysis.

Pyrolysis units integrated with gas chromatography are found commonly in forensic laboratories and could provide a more sensitive technique for the detection of lubricants. Pyrolysis gas chromatography-mass spectrometry (PyGC-MS) has been described for the analysis of high-molecular-weight PDMS in a nonforensic context (9,10). Pyrolysis converts PDMS to cyclic oligomers (Fig. 3), a series of dimethylsiloxanes of increasing molecular weight, beginning with the cyclic trimer (D3), that can be detected using gas chromatography-mass spectrometry (GC-MS) (Table 1). Identification of these cyclic oligomers is based on chain length (3,10–15).

FTIR can be used to identify PEG from an unknown sample. There are, however, some current limiting factors associated with PEG detection. PEG is unlikely to be found in samples taken from a complainant unless they are obtained almost immediately after the alleged act (P. Thompson, personal communication). Owing to the polarity of PEG, it is readily absorbed across membranes. Also, other polar compounds, such as polyvinyl acetate (PVA), are co-extracted from swabs and mask the detection of PEG by FTIR.

GC-MS has been used successfully to analyze PEG in a nonforensic context. Onigbinde et al. (16) analyzed samples of PEG and discriminated between the oligomers within these samples based on their fragmentation. This technique is likely to provide advantages over FTIR due to an increased sensitivity and advanced peak resolution.

Persistence can be described in a forensic context where some form of evidence continues to exist for a period of time. In terms of evidence arising from sexual assault, the period of persistence is from the time of the alleged act to the time the evidence can no longer be detected by standard laboratory protocol. Thompson (2001) detected PDMS in the vagina up to 24 h postcoitus and on a penile swab 50+ h postcoitus using FTIR. PEG had a much shorter persistence period than PDMS. PEG was detected by FTIR in the vagina up to 6 h postcoitus and on the penile swab for no more than 8 h postcoitus (P. Thompson, personal communication). Two casework samples analyzed by the same author showed that PDMS was detected on anal swabs *c.* 7–8 h following intercourse (P. Thompson, personal communication). Maynard et al. (2) reported that PDMS was detected from postcoital swabs for at least 12 h after protected intercourse and PEG had limited detection after an 8-h period.

There are many variables that can alter the persistence of condom lubricants. The most important factors include the systemic absorption of PEG and the removal of PEG through behavioral acitivites, such as washing. Menstruation is also thought to affect the persistence of these lubricants within the vaginal vault (P. Thompson, personal communication).

TABLE 1—*Key cyclic oligomers formed as a result of the pyrolysis of PDMS.*

Compound Name	Molecular Weight	Abbreviation
(Hexamethyl) cyclotrisiloxane	222	D3
(Octamethyl) cyclotetrasiloxane	296	D4
(Decamethyl) cyclopentasiloxane	370	D5
(Dodecamethyl) cyclohexasiloxane	444	D6
(Tetradecamethyl) cycloheptasiloxane	518	D7

Methods

Condom samples were obtained from all of the major distributors and manufacturers in New Zealand. The samples obtained were representative of the market share of all of the major condom brands and subbrands available to consumers. Those brands included were Durex (SSL New Zealand Ltd.), Ansell (EBOS Group Ltd., Christchurch, New Zealand), Gold Knight (Jackson Allison Medical and Surgical Ltd., Auckland, New Zealand), and Sagami. A list of all of the condom samples, along with the lubricant base determined by FTIR, is shown in Table 2. A 200 cSt PDMS standard (Sigma-Aldrich, New Zealand Ltd., Auckland, New Zealand) and a PEG300 standard (Sigma-Aldrich) were used for method development.

PDMS Detection

A Frontier Laboratories PY-2020iD Double-Shot pyrolyzer was used for pyrolysis of PDMS samples. The PY-2020iD is a vertical microfurnace connecting directly to the GC injection port, via a needle interface, for rapid transfer of pyrolysis products to the GC column. The GC-MS instrument was a Shimadzu QP2010 (Shimadzu Corporation Nakagyo-ku, Kyoto, Japan). The methodology in this paper is transferrable to other pyrolysis instruments,

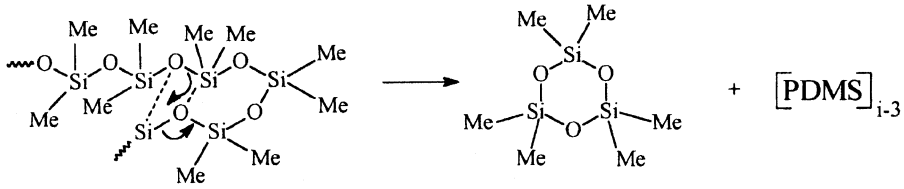

FIG. 3—*Mechanism of the cyclic transition state forming hexamethylcyclotrisiloxane during polydimethylsiloxane thermal degradation (13).*

TABLE 2—*Major condom products on the New Zealand market.*

Brand	Sub-Brand	Lubricant
Durex	Avanti	PDMS
	Classic	PDMS
	Close Fit	PDMS
	Comfort	PDMS
	Confidence	PDMS
	Excita	PDMS
	Extra Confidence	PEG
	Extra Safe	PEG
	Fetherlite	PDMS
	Select—Banana	PDMS
	Select—Orange	PDMS
	Select—Spearmint	PDMS
	Select—Strawberry	PDMS
	Sensation	PDMS
Sagami	Sustaining	PDMS
Gold Knight	Regular	PDMS
	Chocolate	PDMS
	Strawberry	PDMS
	Mint	PDMS
Ansell	LifeStyles Regular	PDMS
	LifeStyles Ribbed	PDMS
	LifeStyles Ultrathin	PDMS
	Mega	PDMS
	Bareback	PDMS
	Exotica	PDMS

provided that the usual validation work is undertaken. The GC contained a 30 m × 0.25 mm (internal diameter) capillary column coated with 5% phenyl silicone (0.25 μm film thickness) and helium as the carrier gas. The instrument parameters were as follows:

Pyrolysis temperature	600°C
Interface temperature	320°C
GC Injector temperature	300°C
GC program	40°C (hold 2 min) to 300°C (hold for 10 min)
	Rate 10°C/min
Split ratio	100:1
MS settings	Electron impact 70 eV
	Ion source 200°C
	MS interface temperature 280°C
	Mode: full scan
	Scan range 29.00–550.00 *m/z*

A dilution series of PDMS standard solutions suspended in hexane was analyzed to establish the detection limits of the PyGC-MS instrument.

Blank cotton-tipped swabs (used in Medical Examination Kits) were loaded with known amounts of PDMS suspended in hexane and left to dry for a minimum of 2 h. The swab extraction followed a protocol similar to previous research (2):

1. The cotton tip was carefully shaved away from the plastic shaft with a sterile scalpel into a small glass vial.
2. 200 μL of hexane (high purity) was added and the cotton tip was manipulated within the solvent. The solvent was removed and added to a fresh glass vial.
3. Steps 1–2 were repeated yielding a total extract of 400 μL.
4. A stream of N_2 (g) was used to evaporate the extract to *c.* 50 μL.
5. The evaporated extract was delivered to a sterile pyrolysis sample cup using a microsyringe.
6. Following complete evaporation of the solvent, the sample was analyzed by PyGC-MS.

TABLE 3—*Condom samples analysed by PyGC-MS.*

Brand	Sub-Brand
Durex	Classic
	Fetherlite
	Sensation
	Select—Banana
	Select—Choc-Orange
Ansell	LifeStyles Regular
	Contempo Mega
Sagami	Sustaining
Gold Knight	Regular
	Mint

A total of 38 blank swabs were analyzed separately along with the loaded swabs to investigate the background matrix and to identify any coextracting substances that may affect PDMS detection. In addition, 15 blank swabs were pooled and extracted together to provide a concentrated profile of a blank swab.

A representative sample of condom products was chosen for PyGC-MS analysis (Table 3). The condom packet was cut open and washed with hexane and the extract was analyzed by PyGC-MS.

PEG Detection

The GC-MS instrument and column were the same as that used for PDMS detection. The temperature program from Onigbinde et al. (16) was altered to decrease the analysis time of each sample.

GC injector temperature	300°C
GC program	40°C (hold 2 min) to 300°C (hold for 10 min)
	Rate 10°C/min
Split ratio	10:1
Autosampler	1 μL injection volume
MS settings	Electron impact 70 eV
	Ion source temperature 200°C
	MS interface temperature 280°C
	Mode: full scan
	Scan range 29.00–550.00 *m/z*

Standard PEG with an average molecular weight of 300 amu (Sigma-Aldrich) was used for all experimentation. A dilution series of PEG suspended in methanol was analyzed to establish the detection limits of the GC-MS instrument.

Loaded unused cotton-tipped swabs were loaded with known amounts of PEG suspended in methanol. A blank methanol standard and blank swabs were analyzed along with PEG-loaded swabs. The swab extraction process outlined previously was repeated using a 4 mL volume of methanol instead of hexane. The suspension is evaporated and resuspended in 100 μL of methanol. The larger extraction volume is used to minimize the possibility of saturation by more polar co-extractants including PVA adhesive. The extracts of the swabs were analyzed by GC-MS to establish the detection limits from loaded unused swabs.

PEG condom lubricant was extracted with methanol from the inside of the condom packet as for the PDMS-lubricated condoms.

Persistence Trial

Two couples took part in this small pilot study. The products distributed were Durex Fetherlite and Durex Select, both lubricated with PDMS. The participants were asked to abstain from sexual intercourse for *c.* 3 days before taking part in the research.

TABLE 4—*Samples collected from participating couples.*

Participant Couple	Product	Postcoital Time (h)	Activity
1	Durex Fetherlite	12	Sleeping
2	Durex Select—Banana	4.5	Sleeping
	Durex Select—Strawberry	9	Sleeping

During this period they were required to take a blank vaginal swab.

Participating couples used the supplied products during sexual intercourse. The participants were supplied with a designated postcoital time period for swab collection. The participants were also asked to include information regarding any significant activity that they undertook during the period between intercourse and swab collection (e.g., showering). Samples were collected by the individuals using a blind sweep method. This method is utilized in casework and involves the taking of an initial swab from the victim before any form of physical examination; thus, no disruption of any residues can occur.

Information regarding products, time periods, and activity was returned with the swabs (Table 4). Both of the participating couples returned blank vaginal swabs collected during the initial abstinence period. Couple 1 returned one postcoital swab and Couple 2 returned two.

A blank sterile swab was extracted along with the vaginal blank and the postcoital swab (Durex Fetherlite) from Couple 1. The extraction protocol described earlier was used and the samples were analyzed by PyGC-MS. The blank sterile swab was analyzed first, followed by the vaginal blank and the postcoital swab. Instrument blanks were run before and after each sample.

The postcoital swabs for Couple 2, blank vaginal swab, and a sterile blank swab were analyzed by PyGC-MS. The analysis followed the same order as Couple 1. The first postcoital swab was from a Durex Select—Banana condom. The second postcoital swab was from a Durex Select—Strawberry condom.

Initial analysis of the postcoital swab from Couple 1 revealed that there was a large amount of PDMS present on the swabs shown by detector saturation of the PyGC-MS instrument. Therefore, the postcoital swab extract was diluted in 1 mL hexane. The loading volume for analysis was 10 µL of the diluted sample. This was also applied to the postcoital swab for Couple 2 (Durex Select—Banana).

Results and Discussion

PyGC-MS

The lowest PDMS standard sample detected was 1 µg. The pyrogram of the 1 µg PDMS sample contained peaks for the D3–D7 cyclic DMS species. The PDMS samples lower than 1 µg could not be conclusively identified due to a lack of peaks in the pyrogram and peaks that could not be identified based on mass spectral fragmentation. Thus, the detection limits of PDMS from standard solutions using PyGC-MS was 1 µg. The pyrogram of a 10 µg PDMS standard solution is shown in Fig. 4, along with the mass spectra for each of the D3–D7 oligomers in Fig. 5. Note that the D8 and D9 species are easily identifiable in this standard based on their mass spectra.

A typical pyrogram for a blank swab is shown in Fig. 6 and a multiple ion chromatogram (MIC) in Fig. 7. The MIC filters for compounds contained the ions at 73, 133, 207, and 281 *m/z*. These are the abundant ions of the cyclic DMS species. The MIC of the blank swab extract contains peaks at positions where peaks of the cyclic DMS species are expected. However, no identification was possible because the concentration was too low, resulting in incomplete mass spectral data.

The MIC of the 15 extracted swabs that were massed together contained peaks that were identified as the cyclic DMS species (Fig. 8). Blank hexane was analyzed by PyGC-MS and contained no peaks for cyclic DMS species; therefore, the swabs must contain trace amounts of PDMS. This is possibly a result of transfer from the industrial machinery used for swab manufacture that may be lubricated with high-molecular-weight PDMS.

The detection limit of PDMS from a loaded unused swab was found to be 1 µg following PyGC-MS analysis (Fig. 9). The D3–D6 cyclic DMS species were successfully identified by the NIST MS library. This is equal to that of the standard solutions, suggesting that the extraction process is satisfactory. The

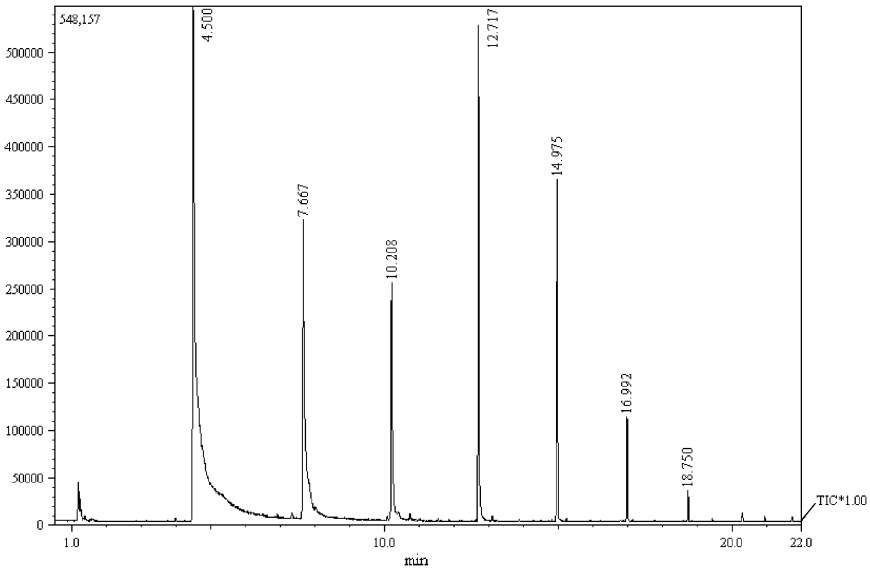

FIG. 4—*Pyrogram of 10 µg standard solution of polydimethylsiloxane in hexane.*

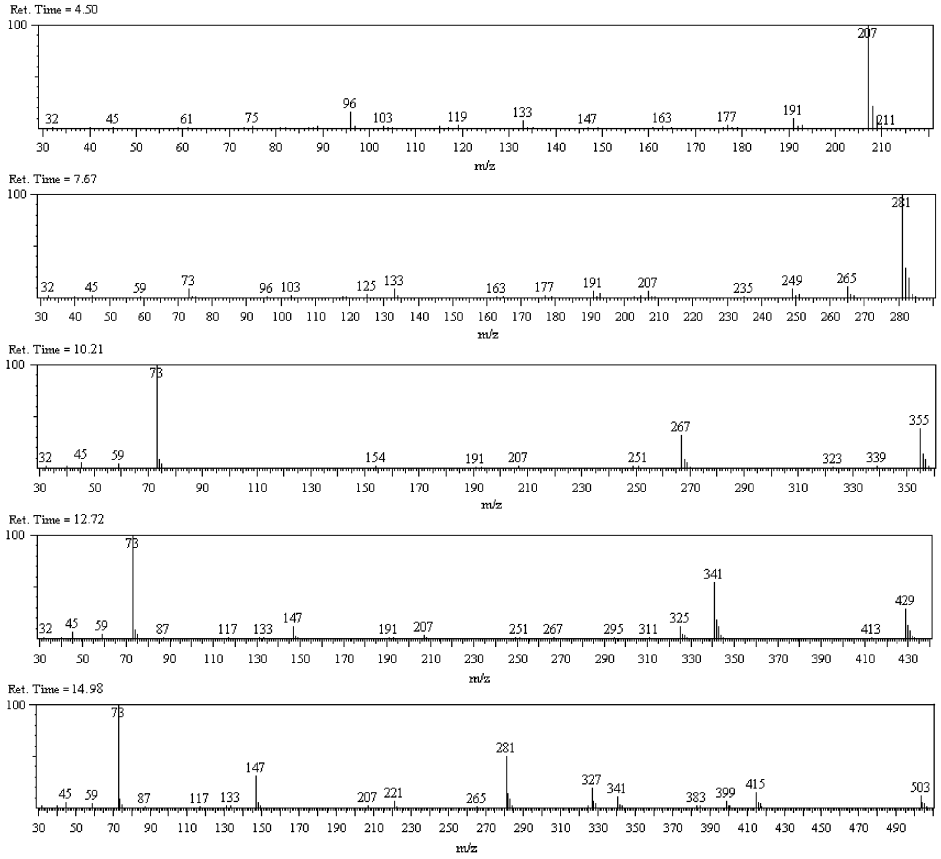

FIG. 5—*Mass spectra of the D3–D7 peaks from Fig. 4.*

instrumental parameters can be altered to increase the sensitivity; however, this should be avoided due to the possible detection of trace levels of background PDMS as demonstrated by the blank swab extractions.

A typical pyrogram from analysis of the 10 condom products is shown in Fig. 10. The pyrograms of the different condom brands and subbrands were all found to be similar. No additional chemical residues were detected in the lubricant formulation following PyGC-MS analysis. PDMS lubricant was clearly detected from all of the sampled products. Further studies using evolved gas analysis (EGA) of the condom packet extracts may provide information about any volatiles that are released at lower temperatures before the pyrolysis temperature. This may provide more detailed information regarding the lubricant formulation used by the dif-

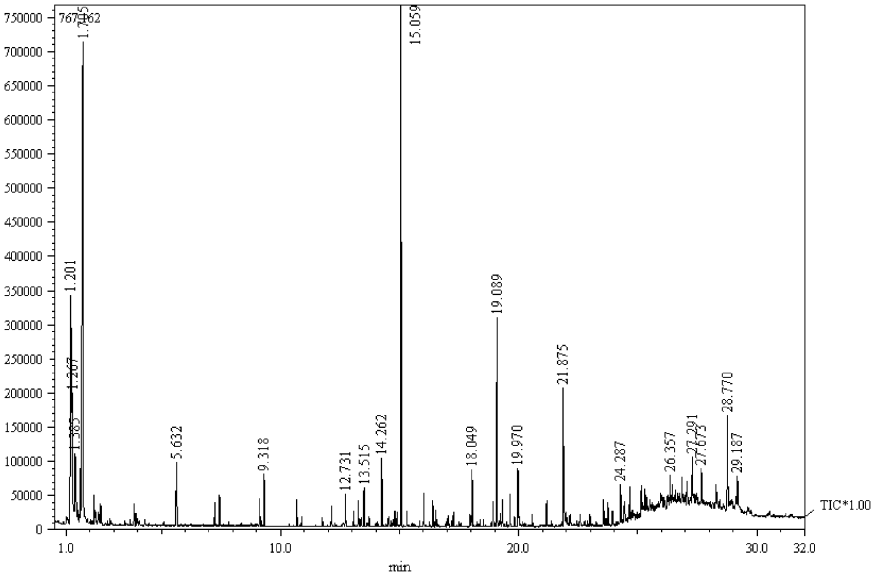

FIG. 6—*Pyrogram of an extracted blank swab.*

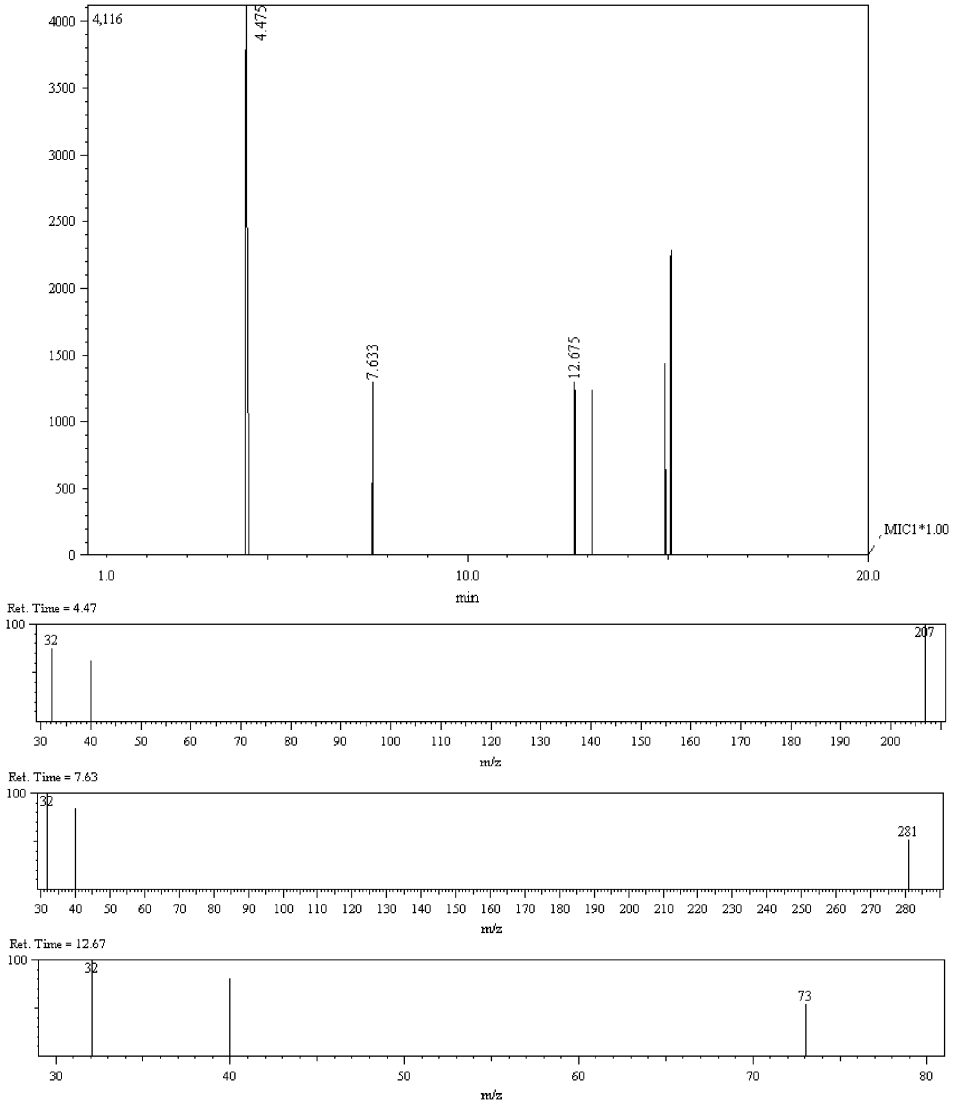

FIG. 7—*Multiple ion chromatograph of an extracted blank swab and MS of the marked peaks.*

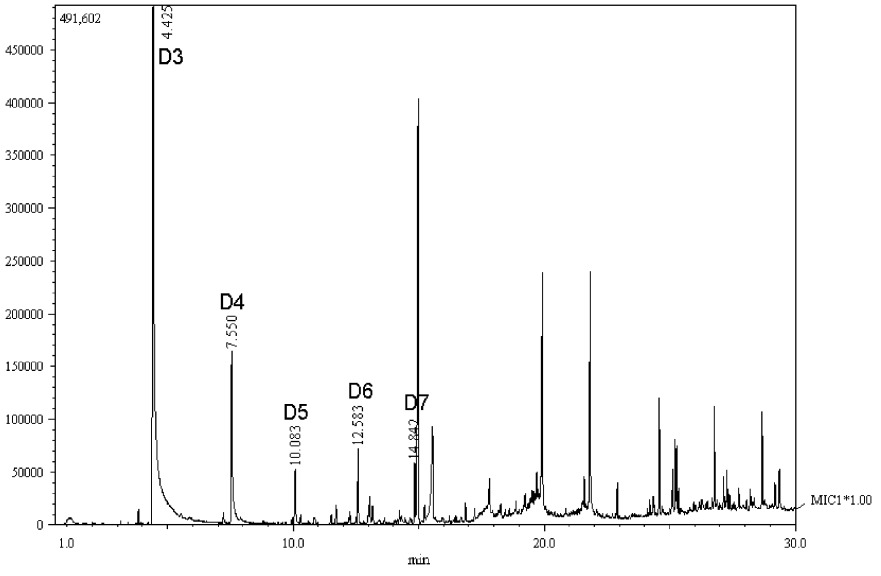

FIG. 8—*Multiple ion chromatograph of 15 extracted blank swabs massed together.*

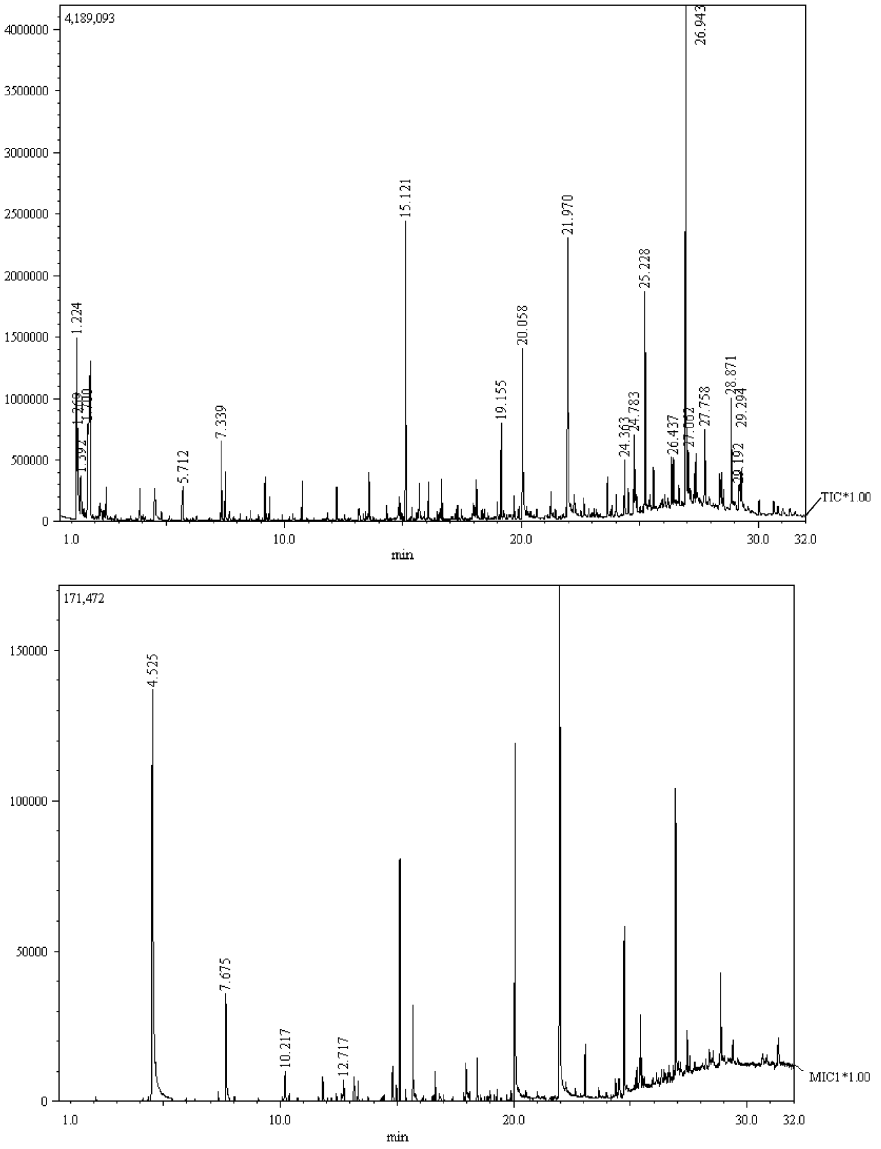

FIG. 9—*(Top) Pyrogram of 1* μg *polydimethylsiloxane-loaded swab; (bottom) Multiple ion chromatograph of 1* μg *polydimethylsiloxane-loaded swab.*

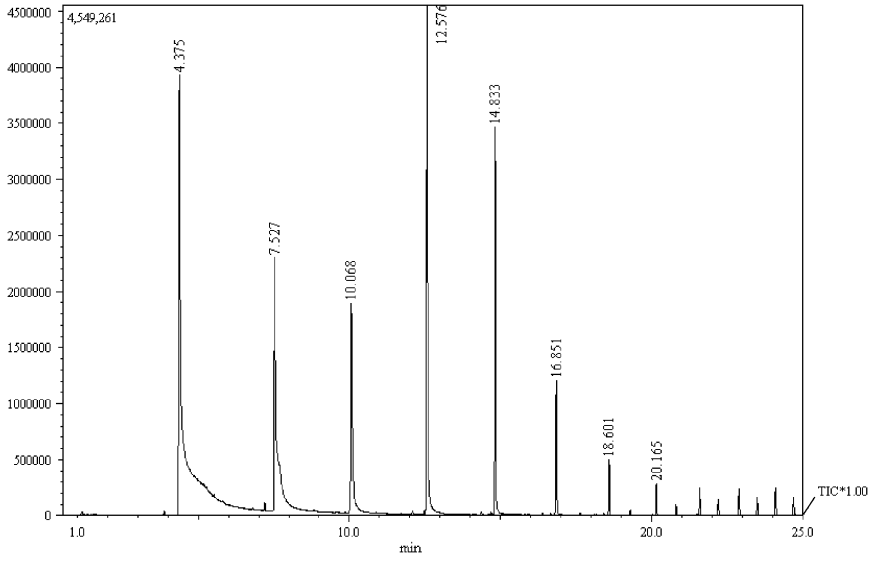

FIG. 10—*Pyrogram of Durex Classic Lubricant.*

ferent manufacturers. However, it is not known whether any lower molecular weight or polar compounds will persist on the body for periods long enough for detection from swabs, especially if they are present at trace levels to begin with.

The PyGC-MS method developed for PDMS analysis was shown to be effective for detection and identification of cyclic DMS products. The most influential parameters were identified as the split ratio and pyrolysis temperature. The split ratio must be set at 100:1 to decrease the residence time in the furnace. This allows for the efficient removal of pyrolysis products from the furnace, minimizing the likelihood of secondary pyrolysis product formation. The pyrolysis temperature should be set at 600°C to ensure optimal degradation of PDMS. Owing to the sensitivity increases over FTIR, and the increased identification capabilities, it is recommended that all nonpolar lubricant extracts be directly analyzed by PyGC-MS.

Pyrolysis Interpretation Criteria

Criteria for elimination and inclusion of unknowns are required for forensic interpretation. Unknown samples should only be included as containing PDMS if these criteria are met, thus minimizing the likelihood of false positives. The criteria described in this section are based on experience gained throughout this research and should provide a method of selection that will exclude any background PDMS from swabs if instrument parameters outlined previously are used. Variations in instrument sensitivity will influence detection. Therefore, it is strongly recommended that detection limits for each instrument are established and a collection of blank swabs are analyzed before implementation into casework.

The pyrolysis products of PDMS, the cyclic DMS oligomers, should be identified in the pyrogram of an unknown sample to conclude PDMS presence. If the sample is a swab extract, MIC analysis should be used. The ions of 73, 133, 207, and 281 *m/z* are good selections for the analysis of the cyclic DMS species.

Identification of the D3 peak should be the first point of inclusion or exclusion. This peak occurs at a retention time of *c*. 4.4–4.5 min. The mass spectrum for the D3 species should include an "isotopic cluster" at 207 *m/z* (M^+), 208 *m/z* (M^{+1}), and 209 *m/z* (M^{+2}). This cluster has been identified previously as a characteristic region of the D3 species (10). If the cluster is present then peaks at 96, 133, and 191 *m/z* should also be identified. If one of these two criteria is not met, the sample can be excluded for PDMS presence. If both criteria are met, then the D3 species is concluded to be present and further peaks can be identified.

TABLE 5—*M^+ and additional ions for each cyclic DMS species.*

Cyclic DMS Species	M^+Ion (*m/z*)	Additional Abundant Ions (*m/z*)
Cyclotrisiloxane (D3)	207	96, 133, 191
Cyclotetrasiloxane (D4)	281	73, 133, 191, 207, 249, 265
Cyclopentasiloxane (D5)	355	73, 267, 268
Cyclohexasiloxane (D6)	429	73, 147, 341
Cycloheptasiloxane (D7)	503	73, 147, 281, 327, 415

The D6 species is a good peak to identify next because it is stable and is usually an abundant pyrolysis product.

When identifying each cyclic DMS species, at a minimum, the mass spectrum should contain the M^+ ion for the corresponding cyclic species and at least three of the additional abundant ions must be located in the mass spectra for each cyclic species (see Table 5). In addition to their presence, the selected ions should be present in similar relative abundance as those of a standard run under the same conditions. If a computer-based library search is available, the peaks may be identified through this method. The percent match for the library searches for each peak must be above 75% and must meet the described criteria of mass spectrum inclusion. The minimum criterion to conclude the presence of PDMS in an unknown sample is the identification of the D3 cyclic species along with at least two other cyclic species within the D3–D7 range. Any samples not meeting these criteria should be eliminated.

GC-MS

The detection limit of PEG from standard solution was concluded to be 0.5 µg. The chromatogram of the 0.5 µg PEG sample

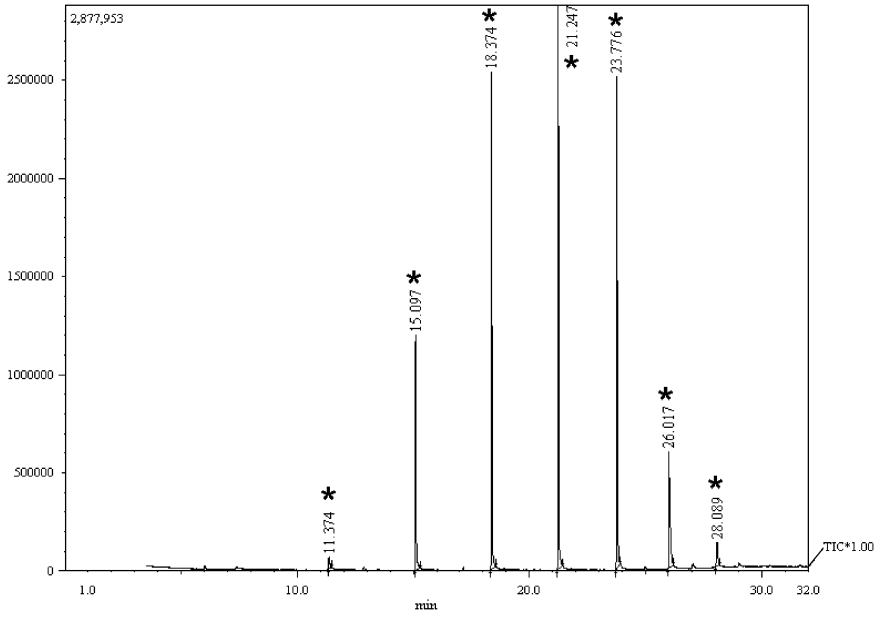

FIG. 11—*1 mg polyethylene glycol swab extract (* marks oligomers).*

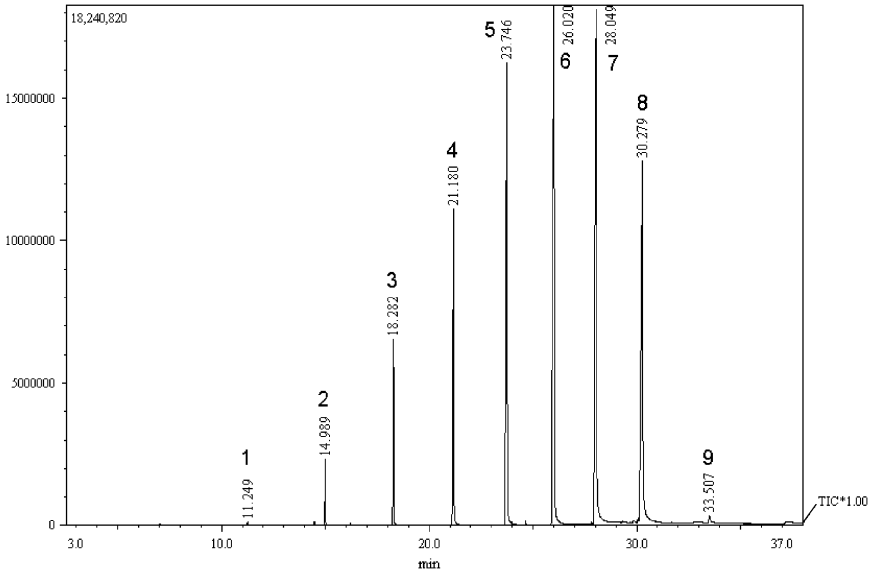

FIG. 12—*Gas chromatogram of Durex Extra Safe lubricant.*

contains peaks corresponding to oligomers from the tetramer up to the nonamer. The triethylene glycol, decaethylene glycol, and undecaethylene glycol peaks are not present in this chromatogram. A 1 mg PEG swab extract is shown in Fig. 11. Please note that this swab was analyzed more recently and on a new colomn with the same packing as all other PEG samples; this accounts for the slightly longer retention times observed in Fig. 11. A standard PEG sample was also run for confirmation.

Blank swabs extracted with methanol did not produce any interfering peaks for PEG detection. The samples of 50, 100, 500 μg, and 1 mg of PEG on loaded unused swabs were all detected by GC-MS analysis. Therefore, the detection limit of PEG from loaded unused swabs was concluded to be 50 μg. It must be noted that the detection limit of PEG from loaded unused swabs, unlike standard solutions, is not the amount of PEG that reaches the GC column for analysis. The evaporated extract is resuspended in 100 μL methanol because the GC-MS autosampler will only function correctly if there is a reasonable level of liquid in the GC vial insert. Therefore, the detection limit from loaded unused swabs should be interpreted as the amount of starting PEG that can be detected from swabs following the method of extraction and analysis set out in this paper.

The gas chromatogram of the Durex Extra Safe extract is shown in Fig. 12. The peaks were identified by comparison with a PEG standard. The peaks marked as 1–9 correspond to PEG oligomers from triethylene glycol ($R_t = 11.249$ min) increasing in chain length to undecaethylene glycol ($R_t = 33.507$ min). The average molecular weight of the Durex Extra Safe lubricant was calculated to be 377.53 amu. This suggests that the Durex lubricant is a PEG formulation closer to PEG350 or PEG400.

The current GC-MS method was shown to be effective for the detection and identification of PEG oligomers. The detection limit from standard solution, 0.5 μg, is 20-fold more sensitive than was found for FTIR (10 μg) (P. Thompson, personal communication). GC-MS is a more sensitive method than FTIR for the detection of PEG. GC-MS analysis also eliminates the need for clean-up pro-

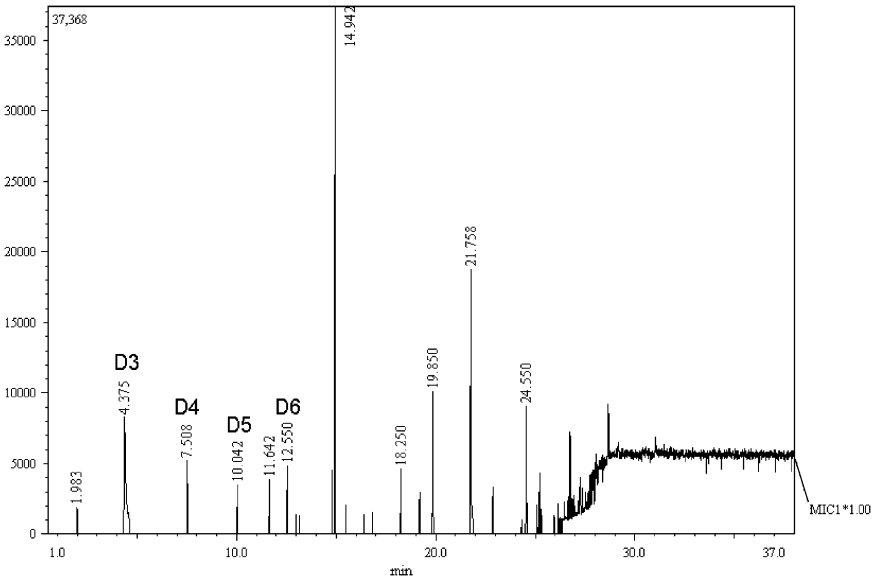

FIG. 13—*Multiple ion chromatogram of the blank vaginal swab from Couple 1.*

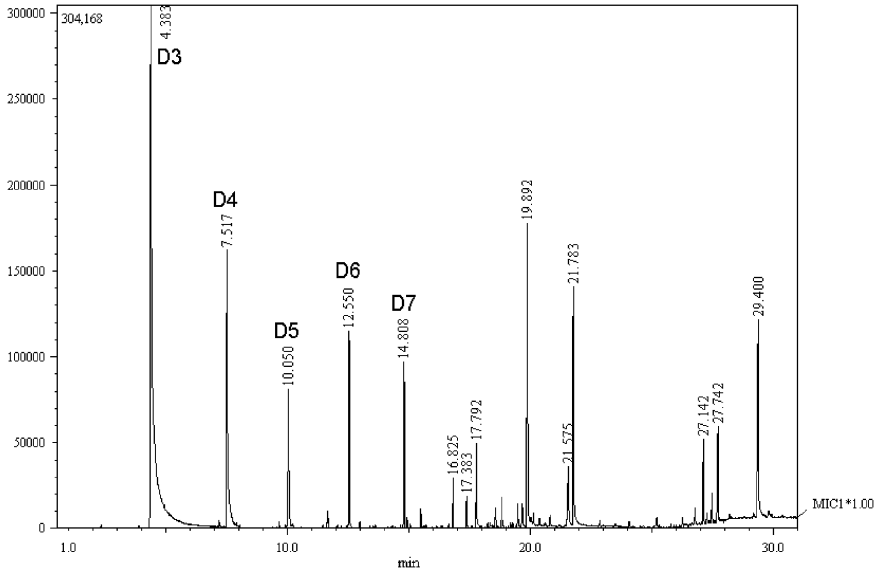

FIG. 14—*Multiple ion chromatogram—postcoital vaginal swab collected 12 h after intercourse with Durex Fetherlite condom (diluted 100-fold).*

cedures to remove PVA from swab extracts because the PEG oligomers are clearly identifiable in the Gas chromatograms. The PEG oligomers are easily identified based on retention time along with comparison with a standard.

The average molecular weight of the PEG sample can be calculated from the peak area information in the gas chromatographs. This information may allow for the discrimination of PEG samples with very different average molecular weights. However, it is believed that case swabs are unlikely to be consistent with the original lubricant solution when considering average molecular weight. It is also believed that the average molecular weight of PEG samples from the same source will be normally distributed. Thus, the analyst is strongly advised not to eliminate samples based on average molecular weight alone. More samples are required, along with statistical analysis, to provide testable parameters for the discrimination of PEG samples based on average molecular weight.

PEG has been shown to have a persistence period of no more than 8 h in the vaginal vault. Because of its polarity, it is thought that the majority of the residual PEG is washed away and absorbed systemically (2). The poor detection limit of PEG from swabs (50 µg), coupled with the short persistence period, suggests that the detection of PEG from postcoital swabs will be limited.

A persistence trial is warranted to determine the time period that PEG can be successfully detected on postcoital swabs using GC-MS. However, at present, the analyst is advised to avoid pursuing the detection of PEG from postcoital swabs if the time delay for swab collection is more than 8 h.

Persistence Trial

(a) Participant Couple 1

The MICs from the analysis of the set of swabs from Couple 1 are shown in Figs. 13 and 14. No PDMS was detected in the blank

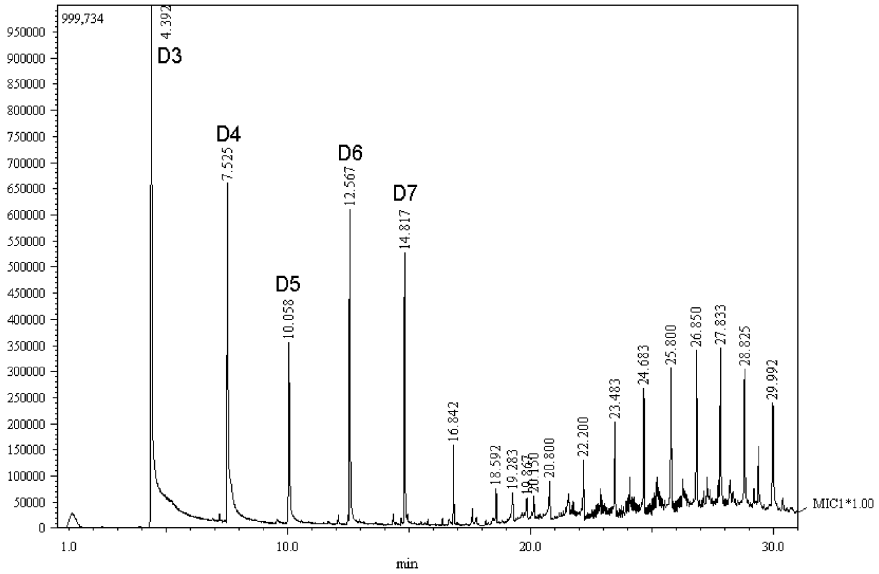

FIG. 15—*Multiple ion chromatogram of postcoital vaginal swab collected 4.5 h after intercourse with Durex Select—Banana condom (diluted 100-fold).*

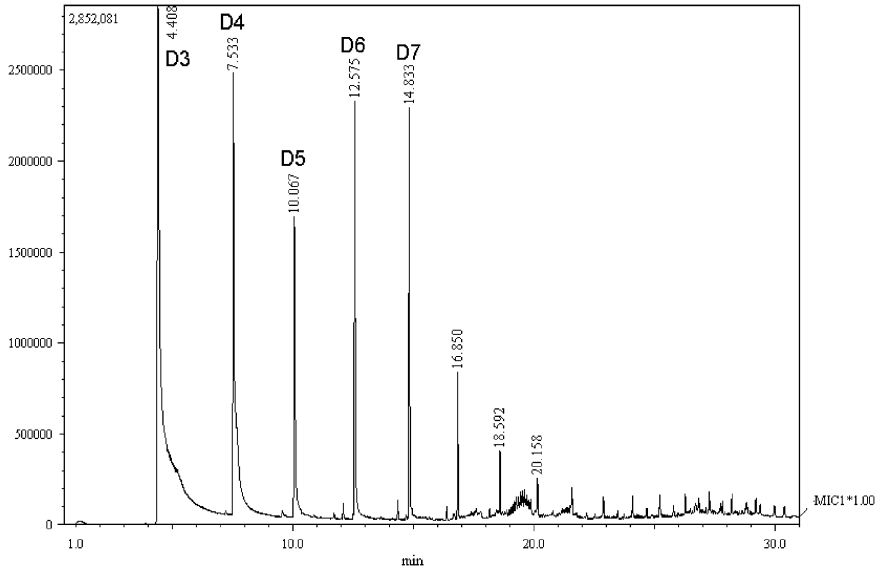

FIG. 16—*Multiple ion chromatogram of postcoital vaginal swab collected 9 h after intercourse with Durex Select—Strawberry condom (undiluted).*

swab; however, minor levels of PDMS were present in the vaginal blank (Fig. 13). This is believed to be carryover from previous protected intercourse. The abstinence period should be increased for future persistence trials to avoid such carryover. The MIC of the 12-h postcoital swab (Fig. 14) contained large peaks that were identified as the cyclic DMS species (D3–D7). The peaks were identified based on their mass spectra and met the predefined criteria. This sample was diluted in 1 mL hexane before analysis (10 µL evaporation volume), a dilution factor of 100.

(b) Participant Couple 2

The MIC of the sterile blank swab and the vaginal blank sample contained no PDMS, when interpreted with the predefined criteria. The vaginal blank sample contained peaks that were indicated by an NIST library search as 2,4-cholestodiene, cholesteryl benzoate, and cholesterol, respectively. These are attributable to vaginal secretions that are co-extracted from the vaginal swabs.

The MIC of the 4.5-h postcoital swab (Fig. 15) contained peaks corresponding to the cyclic DMS species (D3–D7). This sample

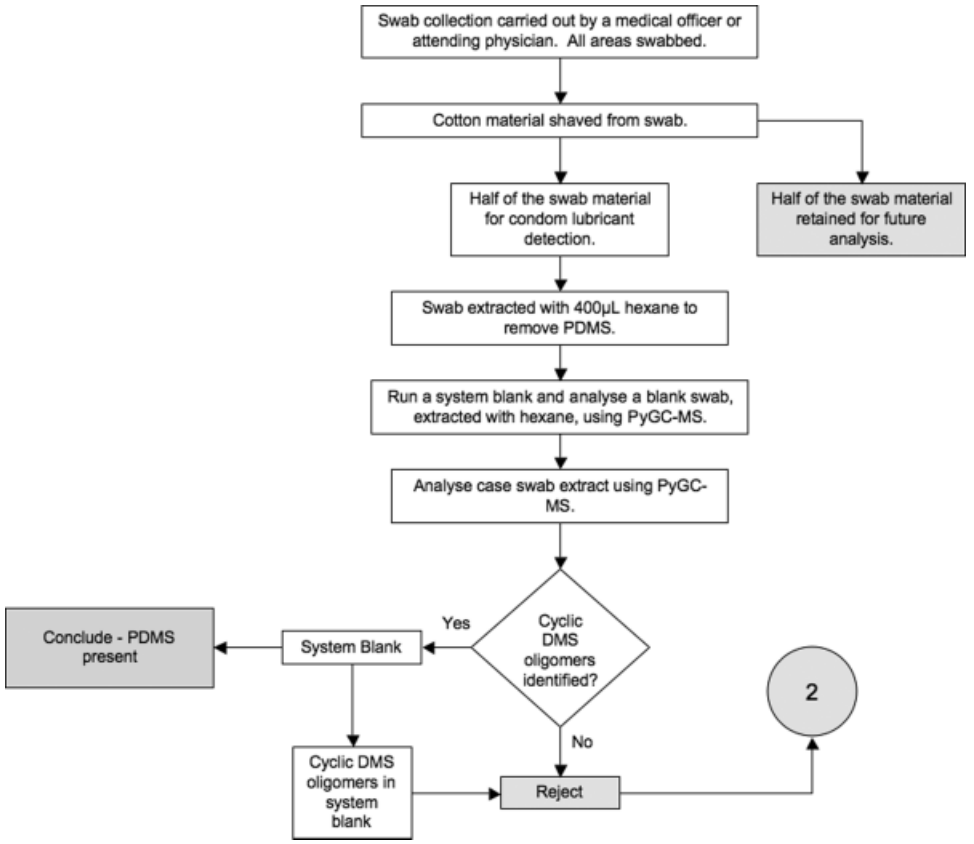

FIG. 17—*Recommended approach for condom lubricant casework.*

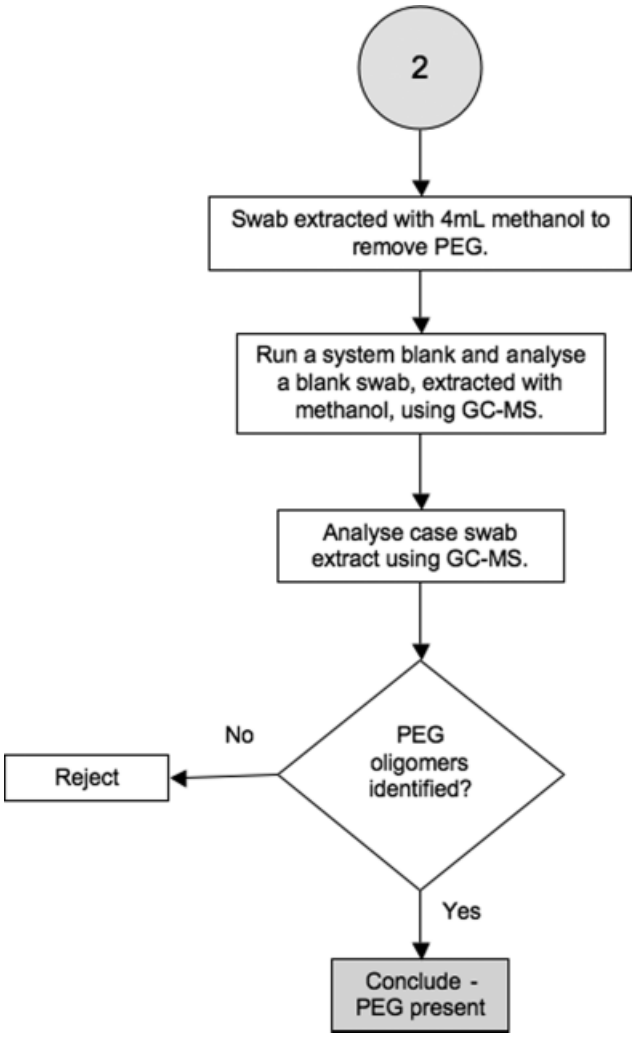

FIG. 18—*Recommended approach for condom lubricant casework continued.*

was diluted in 1 mL hexane. The MIC of the 9- h postcoital swab (Fig. 16) contained peaks corresponding to the cyclic DMS species (D3–D7). Peaks corresponding to cholesterol-like compounds from vaginal secretions did not interfere with the detection of the cyclic DMS species.

PyGC-MS provided effective detection of PDMS from the postcoital swabs. After reasonably long postcoital periods of 9 and 12 h, large amounts of PDMS were detected. Although the actual amount of lubricant was not calculated, an estimation based on the combined peak areas provided a measurable parameter that could be compared with a 10 μg PDMS standard. Only three postcoital swabs were analyzed; thus, no conclusions can be made with regard to the correlation between postcoital period and the amount of PDMS detected. There are practical factors during swab collection that may affect the amount of lubricant collected from the vagina. If someone was particularly thorough when collecting a postcoital swab, they may collect more lubricant than someone who was not. This may also be true for the same person when collecting swab samples at different times.

Casework Recommendations

All of the analyses in this paper were carried out at the Physical Evidence Department at ESR, Mt. Albert, Auckland, New Zealand. It must be stressed that the analyses were structured around the instrumentation available in this laboratory. Therefore, a similar laboratory setup should be used when following the casework recommendations to achieve similar results. The methodology can be applied to other PyGC-MS units following the usual validation procedures.

Cotton-tipped swabs provided in MEKs should be used to swab the vaginal vault, including the vaginal opening, to collect any lubricant present. The surrounding areas should also be swabbed if necessary. The complainant or medical officer may identify other areas that contain lubricant residues. Blank MEK swabs must also be submitted to the forensic laboratory for use as blank controls. These swabs should preferably be from the same batch/kit as the case swabs. This practice will ensure that no misinterpretation occurs. The medical examiners are encouraged to collect swabs initially using a blind sweep method before the use of a speculum to increase the chance of sample recovery.

The time delay of swab collection is one of the limiting factors for lubricant detection. Therefore, the time delay should be noted on the swabs and in relevant correspondence. Any significant activities of the complainant, such as showering, should also be recorded.

All analyses and interpretation should follow the method set out in this paper. A summary of the relevant steps is shown in Figs. 17 and 18.

Conclusions

An effective, sensitive, method for PyGC-MS analysis of the PDMS condom lubricant was established. PDMS was detected to 1 μg from standard solution and from loaded unused swabs. These levels were significantly lower than the detection limits of FTIR. Blank swabs were shown to contain trace levels of PDMS; however, 38 blank swabs were analyzed by PyGC-MS and none produced a pyrogram that was identified as PDMS when the established acceptance criteria was followed. A representative sample of condom products was analyzed by PyGC-MS. All of the condom lubricants analyzed produced similar pyrograms. No additional chemical compounds were identified by PyGC-MS. Therefore, there were no points of discrimination observed between these products when analyzed by PyGC-MS. Overall, PyGC-MS provides an efficient, sensitive method for the qualitative analysis of PDMS lubricant. The ability of PyGC-MS to discriminate between condom brands and subbrands using a single-shot method is limited. PyGC-MS is a technique that shows some advantage over FTIR and its application to casework is recommended. The acceptance criteria established in this paper should always be followed when interpreting casework analyses.

The GC-MS method established was shown to be efficient and sensitive for the detection of PEG. The detection limit of PEG was 0.5 μg from standard solution using GC-MS and 50 μg from swabs using the described method. GC-MS eliminated the need for a cleanup procedure for the removal of PVA adhesive and bodily fluids, as required for FTIR analysis. Durex Extra Safe was the only condom product found to contain the PEG lubricant. This product is repackaged as Durex Extra Confidence for distribution through health professionals. The PEG oligomers were clearly identifiable from GC-MS analysis of the condom extract.

GC-MS is much more sensitive than FTIR and should be used for the analysis of case swabs for the presence of PEG. However, detection of PEG from postcoital swabs is limited by the short persistence period (8 h maximum). The forensic analyst is urged to pursue PEG detection only in cases involving short time delays

or where other circumstances exist that are suggestive of its presence.

A brief lubricant persistence trial was undertaken. PDMS was detected, in abundance, on swabs taken 4.5, 9, and 12 h following protected intercourse.

Recommendations for casework were made to aid the forensic analyst. Using the methods established in this paper, condom lubricant residues can be detected and interpreted as evidence in cases of sexual assault. The findings of such analyses can be confidently presented in a court of law.

Acknowledgments

This research was carried out as part of a Master of Science (Forensic Science) thesis at the University of Auckland, New Zealand. Thanks are due to the Forensic Science program directors Dr. Douglas Elliot and Dr. Gordon Miskelly. Thanks are due to the suppliers, EBOS Group Ltd., Jackson Allison Medical and Surgical Ltd., and SSL New Zealand Ltd., for their kind donation of condom samples and related product information.

References

1. Lee G, Brinch K, Kannangara K, Dawson M, Wilson M. A methodology based on NMR spectroscopy for the forensic analysis of condoms. J Forensic Sci 2001;46(4):808–21.
2. Maynard P, Allwell K, Roux C, Dawson M, Royds D. A protocol for the forensic analysis of condom and personal lubricants found in cases of sexual assault. Forensic Sci Int 2001;124:140–56.
3. Blackledge R. Collection and identification guidelines for traces from latex condoms in sexual assault cases. Crime Lab Digest 1994;21: 140–56.
4. Blackledge R. Viscosity comparisons of polydimethylsiloxane lubricants in latex condom brands via fourier self-deconvolution of their FT-IR spectra. J Forensic Sci 1995;40:467–69.
5. Blackledge R, Vincenti M. Identification of polydimethylsiloxane lubricant traces from latex condoms in cases of sexual assault. J Forensic Sci Soc 1994;34:245–56.
6. Liu M, Maziarz P, Heiler D, Grobe G. Comparitive studies of poly(dimethyl siloxanes) using automated GPC-MALDI-TOF and on-line GPC-ESI-TOF MS. J Am Soc Mass Spectrom 2003;14:195–202.
7. Wolfe J, Exline D. Characterization of condom lubricant components using Raman spectroscopy and Raman chemical imaging. J Forensic Sci 2003;48(5):1065–74.
8. Burger F, Dawson M, Claude R, Maynard P, Doble P, Kirkbride P. Forensic analysis of condom and personal lubricants by capillary electrophoresis. Talanta 2005;67:368–76.
9. Fujimoto S, Ohtani H, Tsuge S. Characterization of polysiloxanes by high-resolution pyrolysis-gas chromatography-mass spectrometry. Fresenius Zeitschrift fur Analytische Chemie 1988;331:342–450.
10. Kleinert J, Weschler C. Pyrolysis gas chromatographic-mass spectrometric identification of polydimethylsiloxanes. Anal Chem 1980;52: 1245–8.
11. Ballistreri A, Garozzo D, Montaudo G. Mass spectral characterization and thermal decomposition mechanism of poly(dimethylsiloxane). Macromolecules 1984;17:1312–5.
12. Camino G, Lomakin S, Lageard M. Thermal polydimethylsiloxane degradation. Part 2. The degradation mechanisms. Polymer 2002;43: 2011.
13. Camino G, Lomakin S, Lazzari M. Polydimethylsiloxane thermal degradation. Part 1. Kinetic aspects. Polymer 2001;42:2395–402.
14. Deshpande G, Rezac M. Kinetic aspects of the thermal degradation of poly(dimethylsiloxane) and poly(dimethyl diphenyl siloxane). Polymer Degradat Stabil 2002;76:17–24.
15. Thomas T, Kendrick T. Thermal analysis of polydimethylsiloxanes. I. Thermal degradation in controlled atmospheres. J Polymer Sci 1969;7(Part A2):537–49.
16. Onigbinde A, Nicol G, Munson B. Gas chromatography/mass spectrometry of polyethylene glycol oligomers. Eur J Mass Spectrom 2001;7: 279–91.

Additional information and reprint requests:
Amanda L. Gordon, M.Sc.(Hons)
C/o ESR Ltd.
Private Bag 92021
Mt. Albert, Auckland
New Zealand
E-mail: amanda.gordon@esr.cri.nz