

TECHNICAL NOTE

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Viscosity Comparisons of Polydimethylsiloxane Lubricants in Latex Condom Brands via Fourier Self-Deconvolution of their FT-IR Spectra

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ABSTRACT: Many brands of latex condoms use a polydimethylsiloxane lubricant. The lubricant viscosity in ten different brands was compared by determining the average chain length through the ratio of the dimethyl to trimethyl peak area obtained after applying the resolution enhancement technique of Fourier self-deconvolution to their diffuse reflectance FT-IR spectra in the area around 800 cm^{-1} .

KEYWORDS: forensic science, sexual assault, deconvolution, polydimethylsiloxane, FT-IR, condoms

Many latex condom manufacturers use as a lubricant a silicone oil, polydimethylsiloxane (PDMS). Forensic laboratories are increasingly receiving evidence from sexual assault cases (rape, forcible sodomy, and child sexual abuse) in which it is alleged that the assailant wore a condom. Lubricated condoms may be preferred for such acts, for the same reasons that lubricants such as petroleum jelly have been used in the past [1].

The identification of condom lubricant traces extracted from evidence items can be valuable associative evidence. Findings may tend to substantiate the claims of either the victim or the suspect; help establish that a crime occurred (the *corpus delicti*), and in some jurisdictions—by showing that penetration occurred, help raise the charge to a higher degree of sexual assault.

Blackledge and Vincenti [2] have detailed a protocol for the recovery of latex condom lubricant traces and their identification. FT-IR and desorption chemical ionization mass spectrometry (DCI-MS) were used for the identification of PDMS and also the spermicide, nonoxynol-9. The presence on some latex condom brands of particulates (starches, lycopodium, talc, finely-powdered silica) has also been reported, along with methods for their characterization [3]. Additionally, general guidelines have been proposed for

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the collection and identification of traces from latex condoms in cases of sexual assault [4].

PDMS has many industrial uses including cosmetic and personal care applications [5]. The finding of PDMS traces on evidence items would have greater evidential value if the method could distinguish PDMS used as a condom lubricant from other potential sources. Of even greater evidential value would be the ability to distinguish the PDMS used by different condom manufacturers, or provided to them by different suppliers, or even from different lot numbers from a given supplier.

Fourier self-deconvolution (FSD) is a method of resolving partially overlapped spectral bands. A discussion of the theory of FSD may be found in the paper by Pierce et al. [6], as well as the references therein. Lipp [7] used FSD to examine the FT-IR spectra of a series of PDMS samples that were pure oligomers. Using FSD in the area around 800 cm^{-1} Lipp was able to separate the peak due to trimethyl groups at the chain ends from the absorption for the dimethyl groups along the chain. A plot of the number of silicon atoms in the chain of each oligomer versus the number obtained for each oligomer when its dimethyl peak area was divided by its trimethyl peak area produced a straight line. Although Lipp only examined pure oligomers, he reasoned that the method could also be used to determine the average chain length of a PDMS mixture.

Since FT-IR is able to identify PDMS traces recovered from evidence items from sexual assaults, FSD applied to the same spectra might show if the viscosity was consistent with that used in condoms, and it might even be able to detect differences in the viscosities used in some brands.

Materials and Methods

PDMS viscosity standards of 50, 100, 200, 350, and 500 cSt were obtained from Hüls America Inc., Piscataway, New Jersey. PDMS condom lubricant samples were obtained from ten different brands. To avoid potential legal problems, specific condom brands tested are not identified, but this is not essential to the findings. The samples designated A through D were from four different U.S. manufacturers, E through G from Japanese manufacturers, sample H from Korea, and samples I and J were different brands from the same German manufacturer. Previous examinations [2] had shown that all ten of the above brands contain PDMS without spermicide.

Condom lubricant samples were obtained by opening a packet and rubbing the condom with a cotton-tipped swab. The cotton was removed from the stick and placed in a test tube and then enough dichloromethane (Omnisolv®, EM Science, Gibbstown, NJ) added to cover the swab. The test tube was agitated for a few seconds with a vortex mixer and then the dichloromethane was removed. To remove any insoluble particulates the dichloromethane extract was filtered through a cotton plug in a disposable pipette.

Although Lipp used a liquid cell and approximately 1% solutions of pure PDMS oligomers in CS₂, liquid cells were not used in the present study due to: 1) their difficulty in cleaning; 2) the toxicity of CS₂ vapors; 3) the fact that when dealing with traces recovered from actual evidence items one would have no idea of the approximate PDMS concentration. In their use of FSD for conformational studies on poly(vinyl chloride), Compton and Maddams [8] used diffuse reflectance as well as other sampling methods.

In this study, samples were examined as one drop of a dilute solution of the PDMS in dichloromethane applied to finely ground KBr in the macro sample cup of a Spectra-Tech "Collector" diffuse reflectance attachment. The drop causes a slight depression on the surface of the KBr. To counteract this, the ground KBr was first added to the sample cup so that it formed a slight dome. After application of the drop a spatula was used to gently flatten and smooth the KBr. For each sample the height of the cup was adjusted for maximum FT-IR alignment signal.

All spectra were obtained with a Nicolet 510P spectrometer equipped with a DTGS detector. The sample compartment was continuously swept with a dry air purge (74-5041 Pure Air Generator, Balston, Inc., Haverhill, MA). Five hundred scans were collected for both sample and background (pure KBr), using Happ-Genzel apodization and 2 cm⁻¹ resolution.

It was important to accurately measure the peak area of the trimethyl band, which becomes smaller in comparison to the area of the dimethyl band as average chain length (viscosity) increases. Therefore the Kubelka-Munk diffuse reflectance correction was not used since it tends to minimize weaker bands [8].

Nicolet software programs were used for FSD calculations as well as peak area measurements. The operator specifies certain parameters and values in the FSD algorithm. For all measurements "FSDAPOD" was set to HAPP-GENZEL, "FSDWIDTH" to 20 cm⁻¹, and "FSDFACTOR" to 2.0. After FSD, before calculating the peak areas it was necessary to add a "FRACTION" to the spectrum so that all values above the baseline would be positive. Before peak area measurements, the software requires the operator to fill in a "Band Specification Table." MEASURE-ONLY was specified for the "BANDMODE" parameter, 2 for "#BANDS," AREA for "METRIC," and TWOPNT for "BASEMODE." For Band 1 (the trimethyl band) 853.00 cm⁻¹ was specified for both "BAND START" and "BASE START," 834.00 cm⁻¹ for both "BAND END" and "BASE END." The corresponding values for Band 2 (the dimethyl band) were 834.00 cm⁻¹ and 773.00 cm⁻¹.

Results and Discussion

After placing a sample in the closed sample compartment it took at least 15 minutes of purge time before spectra without significant contributions from water bands were obtained. This may be because the evaporation of the CH₂Cl₂ on the KBr produced condensation due to cooling. It then took more than five minutes to collect 500 scans at 2 cm⁻¹. This could be speeded up a bit if an MCT detector were available.

Although the time required before obtaining useful spectra is a drawback when examining numerous samples, this would be less of a problem when examining evidence from a typical sexual assault case. Only a few samples would require this type of determination, and the results could then be compared with those previously stored in a computer data base.

Figure 1 shows the spectra between 860 cm⁻¹ and 760 cm⁻¹ for the 50 and 200 cSt PDMS standards before (top) and after (bottom) FSD. FSD is able to split the broad absorption between roughly 853 cm⁻¹ and 773 cm⁻¹ into a trimethyl band centered at about 844 cm⁻¹ and two incompletely-separated bands at about 822 cm⁻¹ and 797 cm⁻¹ that are largely due to the dimethyl groups. As expected, the trimethyl band is smaller than the dimethyl and there is also a comparative decrease in its area as the PDMS viscosity (average chain length) increases.

Table I shows the values obtained after FSD for the dimethyl peak area divided by the trimethyl peak area (2ME/3ME) for the PDMS viscosity standards, and then for the ten condom brands. These are averaged values. Viscosity standards and condom brands were each examined at least three times. FSD was able to distinguish between each of the PDMS viscosity standards. As expected, the 2ME/3ME values increase with increasing chain length. Most of the latex condom brands gave 2ME/3ME values that were not

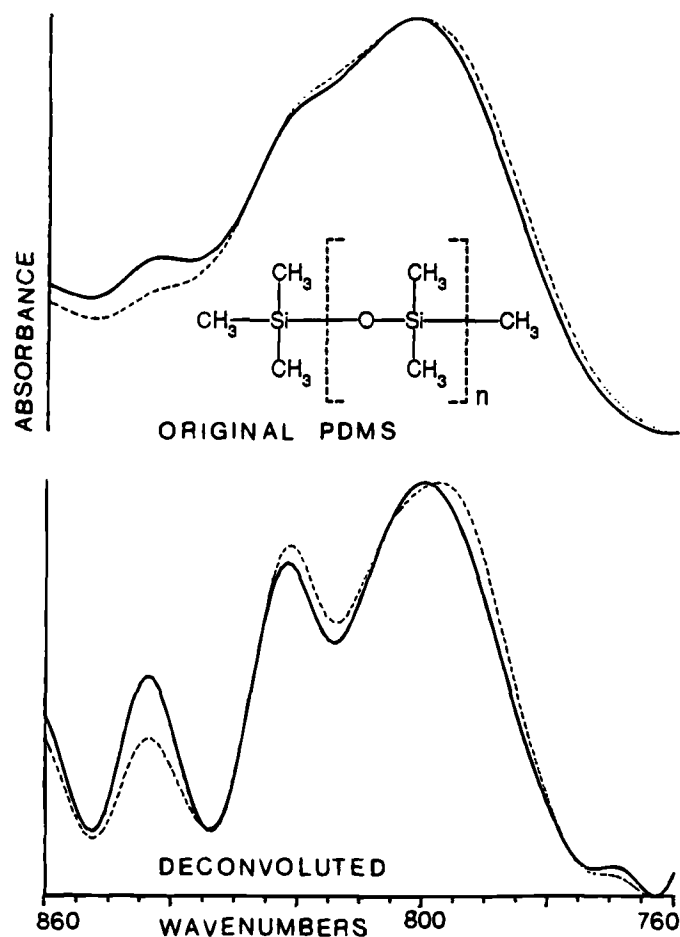


FIG. 1—The original and deconvoluted spectra of the 50 cSt PDMS standard, and the 200 cSt PDMS standard (dashed line). The 2ME/3ME ratios were determined from the deconvoluted spectra by dividing the peak areas above the straight line drawn between 834 cm⁻¹ and 773 cm⁻¹ (dimethyl) by the peak area above the straight line drawn between 853 cm⁻¹ and 834 cm⁻¹ (trimethyl).

TABLE 1—Dimethyltrimethyl peak area ratios.

PDMS standards	Condom Brands	2ME/3ME ^a
50 cSt	F	8.7 ± 0.02
100 cSt		9.8 ± 0.1
200 cSt		10.9 ± 0.2
	D	14.3 ± 0.2
		14.4 ± 0.1
		14.8 ± 0.1
		16.7 ± 0.1
		16.8 ± 0.1
		17.5 ± 0.2
		18.1 ± 0.1
350 cSt	A	20.1 ± 0.1
	G	26.6 ± 0.1
	J	27.0 ± 0.5
500 cSt		27.5 ± 0.8
		33.4 ± 0.8

^aAverage ± standard deviation for at least three replicates.

too far from the 200 cSt viscosity, although sample F is clearly lighter, and samples G and J heavier. It is interesting that viscosity differences were seen in two brands manufactured by the same company, (samples I and J). However, this difference is consistent with the advertising on the condom boxes (greater sensitivity = thinner lubricant, greater safety = thicker lubricant).

Summary

As predicted by Lipp [6], the application of FSD to the FT-IR spectra of mixtures of PDMS oligomers can determine their average chain length (viscosity). The viscosities of the PDMS used in the ten different latex condom brands examined ranged between roughly 100 and 350 cSt. This could possibly be used to determine if the PDMS recovered from evidence items in sexual assault cases is consistent with having originated from a condom, but first, additional studies should address the following questions: (1) are the viscosity values characteristic of a particular brand, or do they vary with the supplier of PDMS to the condom manufacturer, or do they vary according to the lot number from a given supplier? (2) are the viscosity values obtained from post-coitus swabs consistent with the values obtained if the condom packet is opened and directly sampled, or are lighter (or heavier) PDMS fractions more

rapidly lost as vaginal drainage occurs? (3) what viscosity ranges are found in the PDMS used in other commercial products (especially cosmetic and health care products)?

Although FSD showed some discrimination ability, a method which could also show the distribution of oligomers would be even better. Since only a small portion of the extract is usually needed, FT-IR with FSD could be used as a preliminary screen to identify PDMS traces and determine their approximate viscosity. Then a method capable of greater discrimination (possibly gel permeation chromatography or some sampling methods of mass spectrometry), could be used on the remaining sample.

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