Commentary on: Lee GSH, Brinch KM, Kannangara K, Dawson M, Wilson MA. A methodology based on NMR spectroscopy for the forensic analysis of condoms. J Forensic Sci 2001;46(4): 808–21.

Sir:

I read with great interest the paper by Dr. Garry S. Lee et al., "A Methodology Based on NMR Spectroscopy for the Forensic Analysis of Condoms." I believe their NMR method may have potential applications far beyond what even the authors envision. One example is when questions are raised regarding the veracity of DNA evidence. Some recent reports (1–3) have explored the confusion that can arise in DNA evidence when the suspect has attempted to outwit it by selling, exchanging, or mixing semen samples.

With NMR we may now have a simple method (yes, the instrumentation is expensive, but the extraction and method are simple) that in one test can provide a profile of residues one might obtain from different brands of condoms. In one case (1) where there was a seminal fluid stain on the victim's blue jeans, whose DNA did not match that of the suspect, an unused portion of the stain could have been cut-out and extracted with hexane. Some other areas (where no seminal fluid or any other type of stain was visible) of the blue jeans could have been used as controls and extracted separately with hexane. After the hexane had been evaporated off, the residues could have been dissolved in an appropriate NMR solvent and examined. Comparison of the peaks from the controls and the seminal fluid stain would tell us which peaks were due to substances generally present on the jeans (for example, detergent residues) and those that might have been associated with condom traces. It is very unlikely that seminal fluid would interfere with this comparison. It does not interfere with identification by FTIR and/or desorption chemical ionization mass spectrometry (4) of the silicone oil, polydimethylsiloxane (PDMS), after extraction with dichloromethane and hexane is an even less polar solvent.

By comparison with a library of the NMR profiles of various condom brands (the authors correctly point out that such a library would have to be maintained), it might not only be possible to identify various components (PDMS, polyethylene glycol, nonoxynol-9, etc.), but also be feasible to at least profile a condom from a particular manufacturer (even if there were several different brands made by this manufacturer.)

I believe strongly in the potential of this NMR method; however, I do feel it is necessary to point out a small omission in the paper. In the first paragraph at the top of page 809 the authors state: "There are two types of lubricants used on condoms—those based on PDMS and those using polyethylene glycol 400 (PEG)." Actually I am aware of at least two others. Perhaps most Trojan brands (Carter-Wallace) are not available in Australia (the authors only list the "Naturalamb" Trojan brand.) I do not know their exact market share, but various Trojan brands are large sellers in the USA. Although Carter-Wallace uses PDMS in those brands that are advertised as just "lubricated", their chemists feel that PDMS and nonoxynol-9 are incompatible. Therefore in those brands that contain this spermicide, a water-soluble gel-type lubricant is used. This lubricant contains many ingredients, but by far its major one is propylene glycol (please note that this is not the polymer PEG). In addition, I believe there are several brands sold outside the USA that contain glycerol as a lubricant.

This minor correction in no way detracts from the excellence of the paper. In fact, the greater diversity among condom lubricants can only increase the discriminatory value of their NMR method. The many components in the gel-type lubricant used by Carter-Wallace should especially provide a unique NMR signature. Propylene glycol and glycerol are both quite polar and very water-soluble; the authors might wish to try extracting these condoms with a polar solvent and dissolving the residue in a polar NMR solvent.

References

1. Blackledge RD, Letter to the editor: DNA versus fingerprints. J Forensic Sci 1995;40(4):534.
2. Personal communication. Deputy District Attorny Eleanor Hunter, State of California vs David Wayne Arisman, and newspaper stories in the Daily Breeze (Torrance, California) between 26 August 1997 and 16 January 1999.
3. Willing R. Criminal try to outwit DNA, USA Today, 28 Aug. 2000.
4. Blackledge RD, Vincenti M. Identification of polydimethylsiloxane lubricant traces from latex condoms in sexual assault. J Forensic Sci Soc 1994 Oct/Dec;34(4):245–56.

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Authors' Response

Sir,

In a previous paper (1), we examined the technique of solid state and solution nuclear magnetic resonance (NMR) spectroscopy for the forensic analysis of Australian condoms. We presented a methodology that was capable of distinguishing condoms from different manufacturers based mainly on the comparison of the ^1H NMR spectrum (condom spectral fingerprint) of hexane extracted portions. This technique made use of the different compositions of chemical additives, preservatives, spermicides, and lubricants that were added to the condom by the manufacturers.

In his comment of our work, Blackledge (2) has made a number of points. He comments that condom trace evidence can provide clues into crimes in which the suspect has been cunning enough to try and outwit such as buying or exchanging semen by criminals to fool DNA analysis. In our paper we could have listed a myriad of other examples where DNA evidence may be a problem, involving bizarre sexual practices and multiple rapes. However, we wanted to stress the point that of the currently used techniques in the analysis of condom trace evidence, NMR is by far the most successful and useful in discriminating individual brands. It is well established that DNA analysis should not be considered the "be all and end all" of forensic science and our work assists here.

The second point is more implied and was mentioned in our original manuscript. However, it is still worthy of reiterating, i.e., that trace evidence of this kind can assist investigators by providing associative evidence and thus provide a link to the crime or it can aid in proving that a crime did actually occur.

The third point that there exists four types of lubricants and not two is trivial but points to the need to internationalize the work. Our research and personal communications with representatives of various companies revealed that only two lubricants, polydimethylsiloxane (PDMS) and polyethylene glycol 400 (PEG) based, were used at the time of the research in Australian condoms. The Trojan brand by Carter-Wallace, which is said to contain a propylene glycol based lubricant, is not available in Australia. In fact, Carter-Wallace only produces one brand in Australia, Bikini (3), which as afar as we can ascertain is a non-lubricated condom (3). Nevertheless, it was so rare that we were not able to obtain a sample at the time of the investigation. However, this does not mean that a condom, possibly Trojan, or one which contains a glycerol-based lubricant cannot make its way into Australian society. The ease of mail order buying and internet shopping coupled with the many visitors coming into the country at any one time provides plenty of opportunities for these condoms to enter the country. Moreover, propylene glycol and glycerol based lubricants are available in Australia but as additional or separate gels or creams that may be applied to the condom. We also understand that in the course of development, new lubricants and spermicides will be developed and thus have stressed in our original manuscript the need to keep the database updated (a point also agreed on by Blackledge).

To expand this point ad nauseam, in addition to polydimethylsiloxane, polyethylene glycol 400, glycerin and propylene glycol, we also know of attempts to use polypropylene glycol, polyisobutene, polyoxyethylene, behenic acid, behnyl alcohol, sorbitol (4) as well as mixtures of alcohols and acrylic polymers (5–7) as lubricating agents in condoms. Okamoto Industries (who manufacture the Liaison brand) and Sagami Rubber (Duo and Doms brands), both in Japan, have experimented with these new lubricants (5–7). In addition, organometallic zinc compounds are currently being tried as spermicides (4). For completeness, it should also be mentioned that manufacturers such as Sesicon Corporation have produced condoms using new polymer backbones that are yet to be available in Australia. Tactylon from Sesicon Corporation is made from a styrene-ethylene-butylene-styrene polymer, and there are others in the developmental stages that may become available in the near future. It goes without saying that all of these products, when released to the market, must also be included into the database.

Finally, Blackledge also cites an example of a smeared semen stain that may be extracted and tested for components of the condom lubricant. Although he uses this as an illustrative example, this may be construed by those unfamiliar to NMR, that it is a sufficiently powerful enough technique for the analysis of lubricant traces from condoms in semen stains. Unfortunately, currently this is not true. In such small dilute samples, the strong lubricant base may be detected, but the smaller trace components, which distinguish the individual condoms, will not. However, NMR is a versatile technique and many different experiments may be executed to obtain different kinds of information. Work is also currently underway to improve the detection limits for condom trace analysis by NMR, making use of the new pulse field gradient techniques to suppress the strong lubricant and/or solvent signals. Moreover, micro-NMR techniques are now becoming available. These techniques are capable of producing high-resolution spectra from nano-liter volume samples (8,9) giving hope to forensic scientists that analysis of this kind may be possible in the near future.

We reiterate that our paper is a somewhat introductory investigation and covered the popular and easily obtainable condoms in NSW, Australia. Information from the Therapeutic Goods Administration (TGA) details that 21 brands (79 different condoms) are available for retail sale in Australia (3). In our investigation, we have only looked at 38 condoms from 12 of the brands. Further research is currently underway to establish a complete international database with all available condoms, including novelty ones because although they are not Food and Drug Administration (FDA) approved, they can still be used to hide or remove bodily fluids. An international database such as this would be invaluable to forensic scientists. A pattern recognition computer system is also being developed for the database (10).

References

1. Lee GSH, Brinch KM, Kannagara K, Dawson M, Wilson MA. A methodology based on NMR spectroscopy for the forensic analysis of condoms. J Forensic Sci 2001;46(4):808–21.
2. Blackledge RD. Commentary on: Lee GSH, Brinch KM, Kannangara K, Dawson M, Wilson MA. A methodology based on NMR spectroscopy for the forensic analysis of condoms. J Forensic Sci 2001;46(4):808–21.
3. Australian Register of Therapeutic Goods.
4. Kelly PD. Sexual lubricants containing zinc as an anti-viral agent. U.S. Patent 1993:5,208,031.
5. Ooato I. (Sagami Rubber, Japan). Mixtures of alcohols and acrylic polymers as lubricants of condoms. Patent Application: JP 96-172898 19960611.
6. Ooato I. (Sagami Rubber, Japan). Lubricant compositions for condoms. Patent Application: JP 92-213148 19920702.
7. Tsushima K. (Okamoto Industries). A water-soluble lubricant for a condom and a condom spread with this water-soluble lubricant. Patent: EP 97-122426 19971218, US: 6,196,227.
8. Olson DL, Peck TL, Webb AG, Magin RL, Sweedler JV. High resolution microcoil ^1H NMR for mass limited, nanolitre-volume samples. Science 1995;270:1967–70.
9. Lacey ME, Subramanian R, Olson DL, Webb AG, Sweedler JV. High resolution NMR spectroscopy of sample volumes from 1 nL to 10 μL. Chem Rev 1999;99:3133–52.
10. Lee GSH. Unpublished data.

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