



Condom evidence: Characterisation, discrimination and classification of pyrolysis-GC-MS profiles



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ARTICLE INFO

Article history:

Received 6 January 2021

Received in revised form 18 March 2021

Accepted 12 April 2021

Available online 3 May 2021

Keywords:

Chemometrics

Principal component analysis

Silicones

Lubricants

Quadratic discriminant analysis

ABSTRACT

Analysis of condom evidence commonly focusses on the detection of silicone-based lubricants, such as polydimethylsiloxane (PDMS). Although various instruments are used to analyse silicone lubricants, pyrolysis-gas chromatography coupled to mass spectrometry (py-GC-MS) is one of the few instruments that presents immediate applicability to casework. However, considering that this technique detects silicone-based evidence, it is important to evaluate the discrimination potential of the method when applied to various samples. Examination of the variability within a large sample set from an international market is needed to evaluate the most distinguishing compounds likely to be detected in casework. In this study, 70 condoms, personal hygiene products, and lubricants, were analysed using py-GC-MS. Resulting pyrograms were characterised using published spectral databases. Pyrolysates data were extracted and evaluated using multivariate techniques. Qualitative visual inspection of the data, as well as statistical analysis, revealed at least five groups within the dataset. Discrimination was based on four main oligomers, as well as six minor compounds from siloxane degradation. Condom lubricants were found to present a very regular pattern, allowing for the majority of them to be differentiated from personal lubricants.

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1. Introduction

Condom residues are an important evidence type in investigations of sexual assault, and the number of cases where this type of evidence is relevant has increased within the last decade [1]. Evidence recovered is usually linked to the lubricant on the condom, as it is the most abundant trace that transfers during protected intercourse [2–7]. The most common condom lubricant formulation is based on polydimethylsiloxane (PDMS), and is found on over 95% of the condoms from the international market [2,3,6,8–10]. Other common lubricants are water-based formulations containing glycerol, propylene glycol and/or polyethylene glycol (PEG) [11–13]. The candidates for inclusion within condom formulations are regulated by international norms [14–17], which significantly reduces the substances that can be used and hence present within transferred residues. However, the regulations applying to personal lubricants used as intimate products are slightly different, as their use does not imply protection against sexually transmitted diseases and/or pregnancy. It is therefore possible that

personal lubricants may contain PDMS different from that used in condom formulations.

The differentiation of lubricants using Matrix Assisted Laser Desorption Ionisation – Mass Spectrometry (MALDI-MS) was investigated by several authors: Bradshaw et al. in 2011 [18] and in 2013 [19] have illustrated differences within the mass spectra obtained from different brands and models while Spencer et al. in 2011 [4] processed statistical analysis but could not clearly identify any subclasses in populations containing PDMS. Moustafa and Bridge in 2017 also proposed a discrimination model for the differentiation of condoms and personal hygiene products using Direct Analysis in Real Time- Mass Spectrometry (DART-MS) [20]. Their model differentiated samples with different chemical profiles, such as those containing PDMS, glycerol or PEG. They also demonstrated the possibility of differentiating a silicone personal lubricant from a silicone condom lubricant, but the sample size was moderate (n = 36) and the samples were all sourced from the US market. The most recent discrimination model for silicone lubricants was drawn by Baumgarten et al. [9] who used DART-MS for the discrimination of 56 silicone products purchased on the American market. The model was found to be able to distinguish 11 different classes of chemical profiles based on their mass spectral profile. These are the

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only three existing models for the discrimination of sample classes present in the literature. However, the two techniques have not been applied to diluted samples, case simulations or real cases.

In contrast to these two techniques, pyrolysis gas chromatography mass spectrometry (py-GC/MS) was applied in multiple studies for the detection of condom traces in simulated cases, as well as to study the persistence in different matrices [5,7,21]. This is a proven technique, along with Fourier transform infrared (FTIR) spectroscopy, more specifically with DRIFTS-FTIR [3,6,22], and has demonstrated potential applicability to extracted traces and real cases [7]. A recent study by Maurer et al. [23] reported which analytical and pyrolysis conditions were the most adequate for the separation and identification of PDMS, to ensure good reproducibility of the results. Given the lack of discrimination model existing for py-GC/MS, an attempt of discrimination was made [23]. However, the number of samples was too small ($n = 5$) to infer on their discrimination. Given the potential offered by py-GC-MS, it is relevant to investigate its discriminatory power, in order to determine if the technique is able to differentiate samples from different classes that have indistinguishable profiles by infrared spectroscopy. Indeed, as demonstrated by [3,24,25], FTIR spectroscopy is successful at identifying silicone and non-silicone based samples, which in casework would be important to know, in order to use the most relevant method for the analysis of the evidence. Therefore, in casework, the analytical sequence should be constituted of FTIR analysis prior to any chromatographic or mass spectrometry technique [3,24].

The advantage of using py-GC/MS is that large and non-volatile polysiloxanes, which cannot reasonably be analysed by GC/MS otherwise, can be analysed using this instrument. Silicone lubricants, such as PDMS, are the first target of this type of analysis, especially as more than 95% of condoms found on the international market contain PDMS [2,6,8]. It has also been established that glycerol or PEG-type water-based lubricants are easily analysed using GC/MS without requiring pyrolysis [5,26]. Moreover, the pyrolysis of these water-based lubricants does not result in characteristic profiles, probably due to the decomposition to CO_2 and H_2O of the molecules.

During the pyrolysis, PDMS is degraded into cyclic oligomers of low molecular weight (see Fig. 1), called dimethylsiloxanes (DMS) [5]. These DMS oligomers are usually labelled according to the number of silicon atoms in them: the cyclic trimer (IUPAC name: hexamethylcyclotrisiloxane) as presented in Fig. 1, is called D3 and is the smallest and most stable oligomer generated [27]. Pyrolysis generates a range of cyclic oligomers of increasing molecular weight, based on their chain lengths. Their separation through the capillary column is now possible, knowing that they are volatile molecules, which is not the case of pure PDMS. Pyrolysis is therefore often used for the analysis of polysiloxanes [6,23,28–31].

It turns out that the viscosity of the siloxanes, given by the number of repeated $[\text{Si}(\text{CH}_3)\text{-O}]$ units, affects the size of the area of the peaks in the pyrogram: the lower the viscosity, the lower the area [30]. The effect of the pyrolysis temperature is not negligible because the number of pyrolysis products varies if the temperature increases or decreases [23,31–33]. A fairly high temperature must be

applied to obtain the degradation of PDMS [5,27], but not too high otherwise the degradation of PDMS is altered [29].

The aim of this study was therefore to investigate the chemical profile obtained using py-GC-MS on lubricants extracted with hexane, the solvent recommended by Maynard et al. [3]. This has the added benefit of making the samples comparable to expected concentrations arising from the extraction of case samples. Visual examination of the composition of the dataset was undertaken first to attempt a qualitative differentiation of the samples. Chemometrics was then used to evaluate objective discrimination and classifications.

2. Material and methods

2.1. Material and solutions

Hexane (AR grade, Sigma Aldrich, USA) was used as a solvent. Pyrolysis sample holders were Eco-Cups SF and Eco-Sticks SF purchased from Frontier Laboratories. PDMS 200 centiStokes (cSt), with a molecular weight ~ 9430 , obtained from Sigma Aldrich (USA) was diluted in hexane at a concentration of 1 mg/ml.

Samples were obtained from commercially available distributors in Australia, New Zealand and Switzerland. The samples obtained were considered representative of the markets, as they covered major condom brands and sub-brands and were available to consumers. The dataset includes 2 personal hygiene products (PHP), 7 lubricants and 61 condoms, that are all known to contain silicone lubricants. Table 1 presents the list of the samples used in this study.

2.2. Sample preparation and analysis

For py-GC-MS analysis, condoms were opened, unrolled, deposited in a 40 ml glass bottle and covered with 25 ml of hexane. The bottles were then capped and ultrasonicated for 15 min. The extracts were then diluted 10-fold prior to analysis. Liquid samples, such as personal lubricants, were weighed and diluted in hexane to the approximate concentration of the diluted, extracted condom, between 1.5 and 2.5 mg ml^{-1} .

For each sample, 10 μL of the hexane solution was spiked in the stainless-steel cups and left to evaporate prior to analysis. Three replicates were prepared from each condom extract, to account for sample variability, as well as any variation due to the instrumentation and sample preparation. Blanks were run between each analysis to avoid cross contaminations.

For GC-MS analysis, lubricants, creams, oils and personal hygiene products were diluted at a concentration of approximately 1 mg ml^{-1} in the extraction solvent of methanol containing 0.1% diphenylmethane (vol/vol) as an internal standard (IS). Condoms were unrolled and soaked in 20 ml of extraction solvent. All extracts and dilutions were diluted 1:10 (vol/vol) in methanol before analysis. Each sample was analysed on the GC-MS twice from the same extract to account for sample heterogeneity.

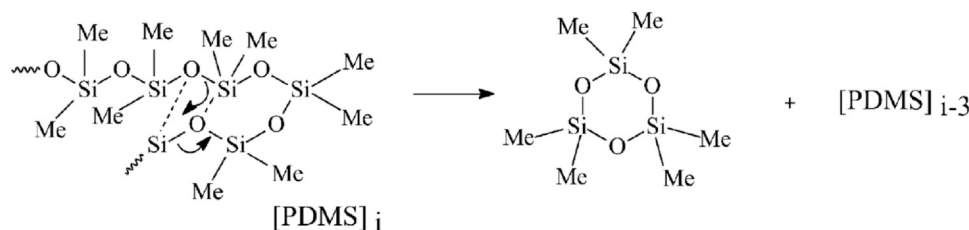


Fig. 1. Pyrolysis of PDMS to produce cyclic oligomers. Reproduced from [29].

Table 1

List of the samples used in the study. Samples were taken from a larger database, which contained multiple samples from the same brand and type. Therefore, replicate samples were removed, thus explaining non consecutive number in the table.

Sample N°	Class	Brand	Type	Country of purchase
1	Condom	Durex	Extra Safe	NZ
10	Condom	Durex	Classic	NZ
11	Condom	Durex	Unknown	NZ
12	Condom	Durex	Pleasure Me	NZ
13	Condom	Shield	XL	NZ
14	Condom	Durex	Mutual Climax	NZ
20	Condom	Durex	Intimate Feel	NZ
23	Condom	Durex	Confidence	NZ
24	Condom	Durex	Banana	NZ
33	Condom	Durex	Apple	NZ
34	Condom	Ansell	Contempo Rough Rider	NZ
36	Condom	Durex	Orange	NZ
38	Condom	Durex	Thin Feel	NZ
40	Condom	Durex	Confidence	NZ
41	Condom	Gold Knight	Chocolate	NZ
42	Condom	Marquis	Flavoured	NZ
44	Condom	Marquis	Regular	NZ
45	Condom	Gold Knight	Strawberry	NZ
47	Condom	Ansell	SKYN-Original	NZ
48	Condom	Ansell	Lifestyles - Ultra Thin	NZ
50	Condom	Ansell	Lifestyles - Regular	NZ
53	Condom	Ansell	Lifestyles - Zero	NZ
54	Condom	Ansell	Lifestyles - Party Variety - Snake Skin Textured	NZ
55	Condom	Ansell	Lifestyles - Party Variety - O'Max	NZ
56	Condom	Ansell	Lifestyles - Party Variety - Tutti Frutti	NZ
58	Condom	Ansell	Lifestyles - Party Variety - Glow in the Dark	NZ
59	Condom	Ansell	SKYN-Elite	NZ
60	Condom	Ansell	Lifestyles - Assorted - Banana Bump Studded	NZ
61	Condom	Ansell	Lifestyles - Assorted - Sonic Strawberry Ribbed	NZ
62	Condom	Ansell	Lifestyles - Assorted - Berry Blast Smooth	NZ
63	Condom	Ansell	Lifestyles - Assorted - Vanilla Thriller Smooth	NZ
64	Condom	Ansell	Lifestyles - Assorted - Choc Ripple Ribbed	NZ
65	Condom	Ansell	Lifestyles - Assorted - Mintensity Studded	NZ
66	Condom	Ansell	Lifestyles - Assorted - Sonic Berry Ribbed	NZ
68	Condom	Ansell	Lifestyles - Party Mix - Choc Ripple Ribbed	NZ
69	Condom	Ansell	Lifestyles - Party Mix - Dynamint Studded	NZ
79	Condom	Durex	Performa	NZ
109	Condom	Ansell	LifeStyles Luxe Silicone-based lubricant	AUS
110	Condom	Ansell	Manix Contact	CH
111	Condom	Ansell	Manix Natural	CH
112	Condom	Ansell	Manix Orgazmax Plus	CH
113	Condom	Ansell	Manix Endurance	CH
114	Condom	Ansell	Manix Fraise Gourmande	CH
115	Condom	Ansell	Manix Xtra Pleasure	CH
116	Condom	FairSquared	Sensitive dry	CH
117	Condom	FairSquared	Original	CH
118	Condom	FairSquared	Max Perform	CH
119	Condom	Migros	M-Budget	CH
120	Condom	Migros	Cosano Regular	CH
121	Condom	Migros	Cosano Sensual	CH
122	Condom	Migros	Cosano Feeling 0.05 mm	CH
123	Condom	Coop	Prix Garantie	CH
124	Condom	Ceylor	Gold	CH
125	Condom	Ceylor	Thin Sensation	CH
126	Condom	Ceylor	Non-Latex UltraThin	CH
127	Condom	Ceylor	Strawberry	CH
130	Condom	Durex	Strawberry	CH
133	Lubricant	Ansell	SKYN Maximum Performance Lubricant	CH
156	PHP	Femfresh	Feminine deodorant spray	AUS
158	PHP	Vagisil	Soothing Oatmeal Cream	AUS
168	Lubricant	Ansell	Skyn Intimate Moments	AUS
169	Condom	Ansell	Skyn Intense Feel Non-Latex Condoms	AUS
171	Lubricant	Astroglide	Diamond Silicone Gel Personal Lubricant	AUS
172	Lubricant	Astroglide	Gel Personal Lubricant	AUS
174	Lubricant	Astroglide	Waterproof Silicone Liquid	AUS
177	Lubricant	Astroglide	Strawberry Liquid Personal Lubricant	AUS
178	Condom	Four Seasons	Naked Black Condom	AUS
179	Condom	Four Seasons	Stubbed & ribbed Stimulating condoms	AUS
180	Condom	Checkmate	ExtraSensitive Lubricated Condoms	AUS
181	Lubricant	Durex	Play Perfect Glide	AUS
184	Condom	Ansell	LifeStyles Ribbed Condoms	AUS

2.3. Instrumental conditions

2.3.1. Pyrolysis-GC-MS

Analyses were carried out using an isothermal oven Frontier Lab py-3030S single shot pyrolyzer device coupled to an Agilent GC 7890B system, interfaced with an Agilent 5977N mass spectrum detector. Software used were respectively Py3030S Control (v. 1.77) from Frontier Laboratories and ChemStation v. F.01.03.2357 from Agilent. Pyrolysis was undertaken at 720 °C for 20 s, under an inert atmosphere, helium as carrier gas.

Separation was achieved on a HP-5MS capillary column (30 m x 0.25 mm x 0.25 µm) using helium as a carrier gas, at a flow rate of 1 ml/min. Injections were carried out in splitless mode, the injector temperature being set at 280 °C. The chromatographic programme was as follows: held at 50 °C for 2 min, increased at 10 °C/min to 230 °C, then 20 °C/min to 300 °C, then held for 5 min at 300 °C, making a total acquisition time of approximately 29 min. Considering mass spectral detection, the transfer line was set at 250 °C, the ion source at 230 °C and the quadrupole at 150 °C. Data were acquired in full scan mode (30–550 *m/z*), with a sampling rate of 3.

2.3.2. Attenuated total reflectance (ATR)-FTIR

Infrared spectra were collected using a Nicolet iS50 FTIR spectrometer equipped with single-bounce diamond crystal ATR accessory. Data collection was carried out using the OMNIC software. Spectra were collected over the 4000–400 *cm*⁻¹ range with 4 *cm*⁻¹ resolution and 32 co-added scans. ATR correction was performed on all spectra to account for variations in penetration depth based upon wavelength.

Condoms were rubbed directly on the ATR crystal and analysed with no further preparation. All other products were applied as thin films to cover the ATR crystal and analysed with no further preparation. The sampling window was thoroughly cleaned using ethanol and lint-free tissue before each sample, and a background scan of the clean crystal was obtained between each replicate

acquisition. For each sample, 5 replicates were acquired, to be able to statistically consider any sample variation.

2.4. Data processing

2.4.1. Qualitative analysis

Identification of the compounds was undertaken using three different mass spectral databases; NIST18 (*National Institute of Standards and Technology*), PP (*Pyrolysis Products*, in-house pyrolysis library) [34–36] and TOX3 (*Wiley Drug and Pesticides*, Wiley138), as well as comparison with retention time and mass spectra obtained from the analysis of bulk PDMS (Fig. 2), and published literature. However, the identification of pyrolysates is a difficult task as pyrograms are complex with numerous peaks. There were some compounds that were not identified using this methodology, and therefore are referred to as “Unknown” followed by their retention time.

Using Agilent ChemStation® software, areas of the target ions within all the acquired pyrograms were integrated for each peak. Peaks were selected as to be repeatable, and distinguishable from the background, over a threshold value of 30,000 A.U. Table 2 references the peaks and their parameters. Data were exported to Microsoft Excel, the whole dataset was normalised to the area sum, and the double square root was calculated prior to multivariate statistical processing.

2.4.2. Chemometrics

Principal component analysis (PCA) was undertaken on the normalised data, using the non-iterative partial least squares (NIPALS) algorithm. Three dimensional scores plots were used to visually explore the data structure and to assess the loadings of the main components. Firstly, groupings related to class (i.e. condom, lubricant, PHP) were examined, to determine if separations were clear or if overlaps between classes existed. The loadings plots related to these sample scores were evaluated to understand the variables most important for sample discrimination and to

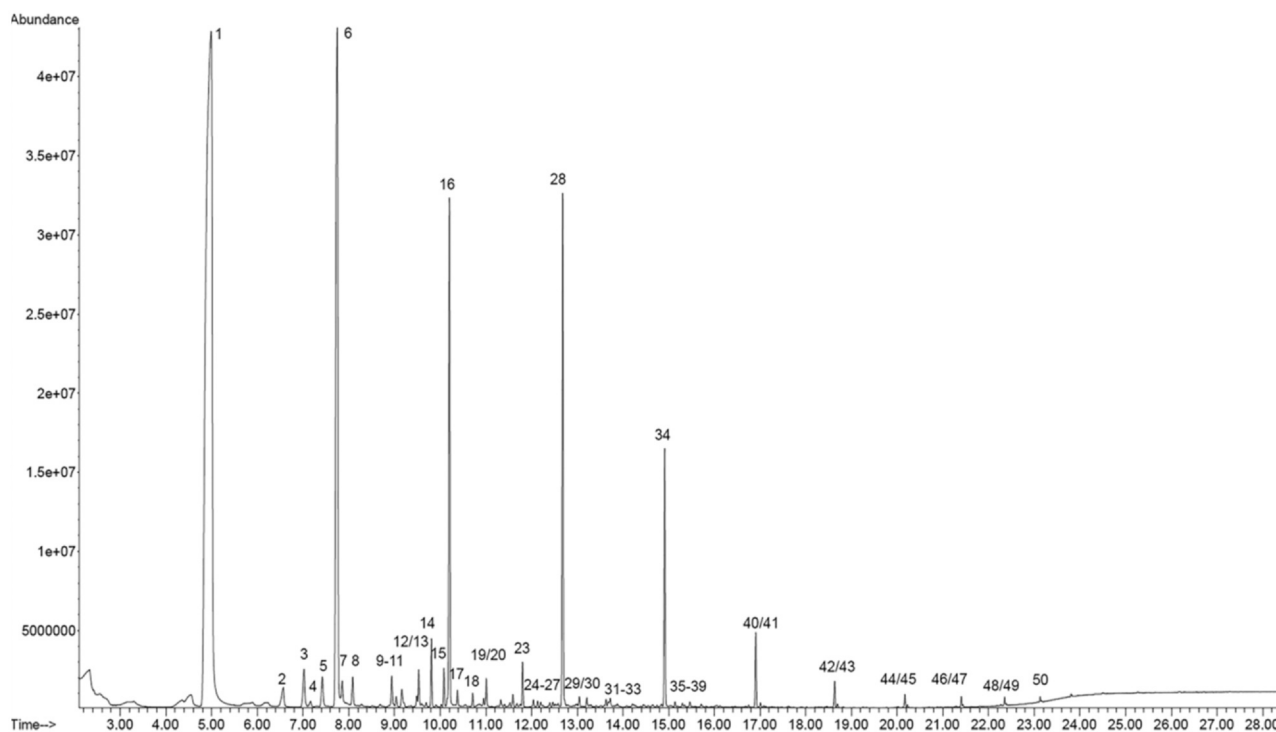


Fig. 2. Chromatographic pattern of PDMS 200 cSt reference, analysed under optimised conditions. Compounds were selected to create the extraction macro. Compound numbers relate to Table 2.

Table 2

Compounds selected for comparison. Names in brackets are suggestions for compounds that were not identified using databases or literature. Qualifiers are listed following their abundance ratio to target ion.

N°	Name	RT (min)	Target ion (m/z)	Qualifiers (m/z)
1	D3	4.93	207	191, 133, 96
2	(linear D3)	6.56	207	193, 221, 177
3	Unknown 7.02	7.02	192	209, 97, 134
4	Unknown 7.16	7.16	267	193, 207, 281
5	Unknown 7.41	7.41	207	223, 191, 133
6	D4	7.73	281	265, 191, 249
7	Unknown 7.86	7.86	267	281, 250, 126
8	(linear D4)	8.08	281	265, 207, 133
9	Unknown 8.94	8.94	265	125, 249, 191
10	Unknown 9.03	9.03	207	193, 247, 176
11	Unknown 9.16	9.16	281	295, 233, 193
12	Unknown 9.48	9.48	267	250, 192, 126
13	Unknown 9.53	9.53	267	126, 250, 283
14	Unknown 9.80	9.80	341	325, 163, 73
15	Unknown 10.08	10.08	341	325, 163, 73
16	D5	10.21	355	267, 73, 251
17	(linear D5)	10.37	355	267, 250, 73
18	Unknown 10.71	10.71	355	267, 250, 73
19	Unknown 10.95	10.95	339	323, 162, 128
20	Unknown 11.00	11.00	339	323, 162, 154
21	Unknown 11.32	11.32	281	339, 267, 321
22	Unknown 11.59	11.59	341	324,163,73
23	Unknown 11.80	11.80	326	415, 73, 399
24	Unknown 12.04	12.04	326	415, 73, 398
25	Unknown 12.19	12.19	326	399, 415, 73
26	Unknown 12.40	12.40	326	415, 269, 253
27	Unknown 12.46	12.46	401	341, 429, 73
28	D6	12.67	341	429, 325, 147
29	(linear D6)	13.04	341	324, 429, 147
30	Unknown 13.21	13.21	413	324, 399, 73
31	Unknown 13.63	13.63	400	489, 326, 384
32	Unknown 13.67	13.67	324	413, 207, 190
33	Unknown 13.72	13.72	400	489, 326, 384
34	D7	14.90	415	281, 147, 326
35	(linear D7)	15.14	503	415, 147, 281
36	Unknown 15.29	15.29	399	487, 325, 147
37	Unknown 15.46	15.46	487	399, 147, 281
38	Unknown 15.71	15.71	475	147, 73, 400
39	Unknown 16.74	16.74	73	147, 221,281
40	D8	16.90	355	401, 281, 221
41	(linear D8)	17.00	221	147, 281, 355
42	D9	18.62	429	355, 221, 147
43	(linear D9)	18.70	221	355, 147, 429
44	D10	20.17	503	281, 355, 147
45	(linear D10)	20.23	533	281, 221, 147
46	D11	21.40	355	535, 147, 281
47	(linear D11)	21.44	429	355, 207, 281
48	D12	22.35	429	355, 207, 147
49	(linear D12)	22.38	207	281, 355, 429
50	D13	23.12	207	281, 355, 429

investigate the potential reduction in the number of variables. Finally, quadratic discriminant analysis (QDA) was undertaken on the entire dataset to build the classification model. Each variable was assumed to have equal a priori probabilities, with a variable weight of 1.0 for each variable. Both PCA and QDA were performed using the Unscrambler X v. 10.5 (Camo Software, Norway).

3. Results and discussion

3.1. Qualitative analysis

All of the samples were analysed in triplicate and the pyrograms were found to be repeatable between replicates in relation to the number of compounds detected, retention times and relative intensities. No major visual differences were noted in the pyrograms of the condom extracts. However, before the appearance of compound D3, i.e. before 4.9 min, peaks of hexan-2,5-dione were identified with a high-quality ranking in the databases. They were found not to

be reproducible between replicates. Non evaporated samples were run and their chemical profile was compared to the one of evaporated samples to investigate if this compound could originate from a solvent issue. Chemical profile were found to be affected if the evaporation was incomplete (data shown in Supplementary Information). It is therefore possible to state that this is more likely that this compound is derived from the pyrolysis and recombination of hexane and hence, was likely due to the solvent not sufficiently evaporating prior to pyrolysis, than from any other compounds pyrolysis.

Peaks that were repeatable in the condom samples were characterised using the various databases available as well as published literature. Up to 50 compounds were found in the chromatographic pattern obtained from PDMS 200 cSt (Fig. 2), with 10 of them being identified as cyclic oligomers generated during the pyrolysis of PDMS, i.e. D3-D13. The remaining 40 compounds could not be conclusively identified, as was mentioned previously. However, by examining the mass spectra and the literature [37] these compounds were consistent with originating from siloxane degradations, and not from other compounds. The retention time and mass spectra were repeatable enough to be used to ensure a proper integration of the compounds. The %RSD for the integrated abundance of the chromatographic peaks in TIC mode were found to be lower than 5% for most of the compounds. Table 2 lists the 50 compounds integrated and extracted for further statistical analysis.

The study of the pyrograms obtained for the 70 samples analysed revealed at least 6 different profiles, which are illustrated in Fig. 3 respectively, amongst a population which presented undistinguished patterns when run in ATR-FTIR (data not shown). Although condom samples did not present any significant visual differences in their chemical profiles, personal lubricants were found to produce different profiles. Most condoms presented a pattern as illustrated in Fig. 3A, with the exception of two condoms, Ceylor Gold and Fair-Squared Sensitive Dry, which presented slightly different chemical profiles, including the presence of PDMS oligomers (Fig. 3B). These condoms were however already differentiated using their FTIR spectra (data not shown) but were run to confirm the observation. Further investigation showed these profiles differed due to terminated silicones, with methylterminated silicones present in Fig. 3A and hydroxyterminated silicones present in Fig. 3B. Amongst the silicone-containing personal lubricant populations, four different profiles were observed, one of them being indistinguishable to condom pyrograms (Fig. 3A) and the three others being visually discriminated (Fig. 3C–E) based on the presence or absence of peaks in the pyrograms. The sixth reported profile (Fig. 3F) was observed for the FemFresh sample, which indicates that this either did not contain a silicone lubricant, or it was present below the limit of detection.

The observation of these different profiles within a population of silicone-based products is an important point to consider. From a qualitative point of view, condom presented two types of profiles according to silicone content. Methylterminated-silicone lubricated condoms presented indistinguishable chromatographic profiles as presented in Fig. 3A. Multiple condom brands chromatograms are gathered in Supplementary Information. Some condoms presented hydroxyterminated silicone lubricant, which allowed the distinction due to a different distribution pattern. Other sources presented different profiles based on the presence or absence of given components in the pyrograms (Fig. 3C). Chromatographic patterns of major cyclic oligomers observed in Fig. 3C and E were very similar. The main difference between these two patterns was due to the minor compounds present, which differed either in terms of presence or absence of peaks, or in terms of relative abundance. Most of the samples contained the same oligomeric degradation pattern, from D3-D6, and the major variations were within the rest of the oligomers (D7-D13), as well as in the minor compounds detected. Fig. 3D also a huge

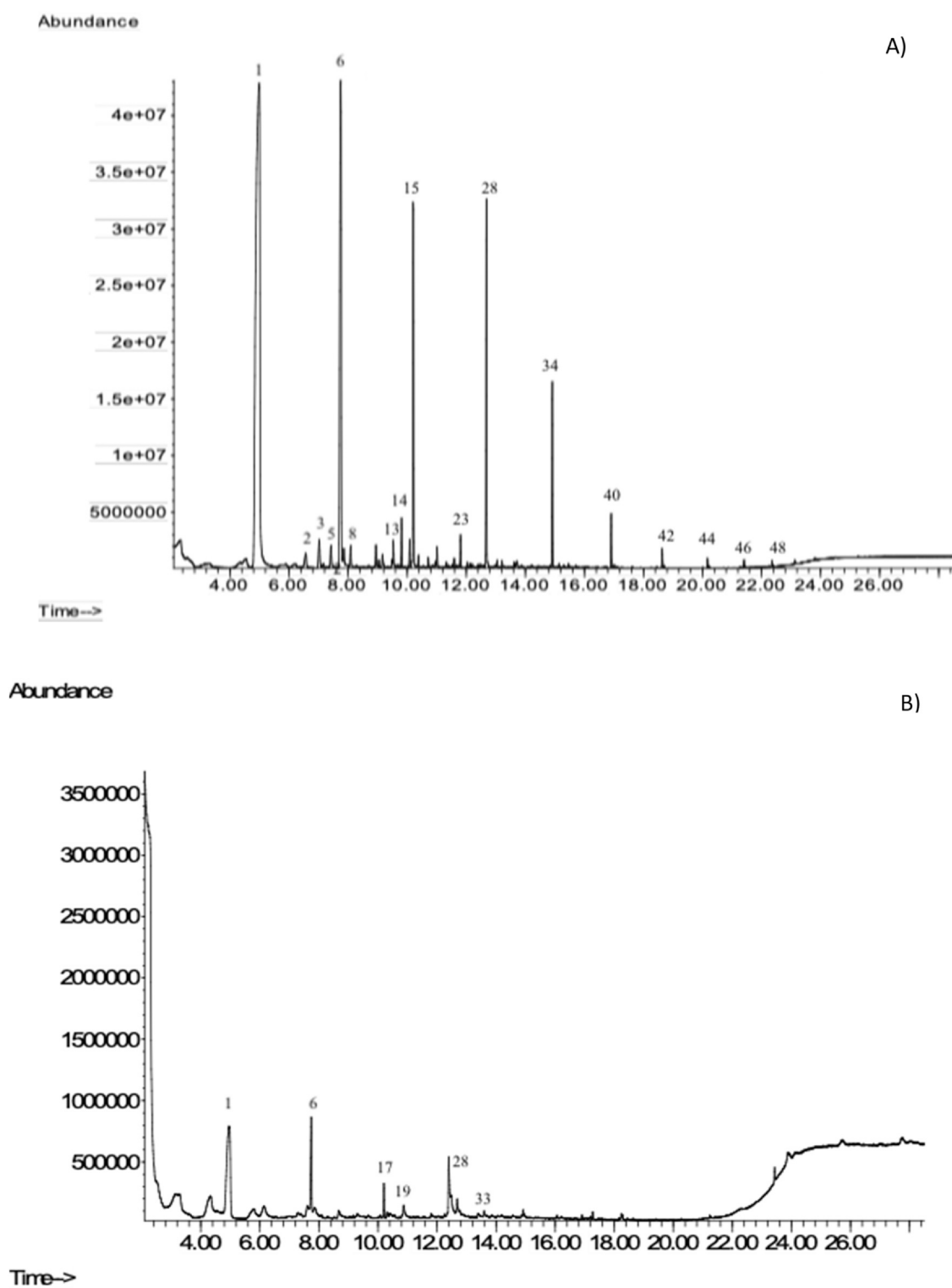


Fig. 3. Illustration of the different chemical profiles observed amongst the dataset. (A) Condom profile (Sample 01-Durex Classic)- methylterminated silicone, (B) condom profile (Sample 124-Ceylor Gold) – hydroxyterminated silicone, (C) lubricant type 1 profile (Sample 109 - Ansell LifeStyles Luxe Silicone-based lubricant), (D) lubricant type 2 profile (Sample 171 - Astroglide Diamond Silicone Gel Personal Lubricant), (E) lubricant type 3 profile (Sample 174 - Astroglide Waterproof Silicone Liquid), (F) profile obtained for Sample 156 - FemFresh Feminine deodorant. Some compounds are annotated with numbers corresponding to [Table 2](#).

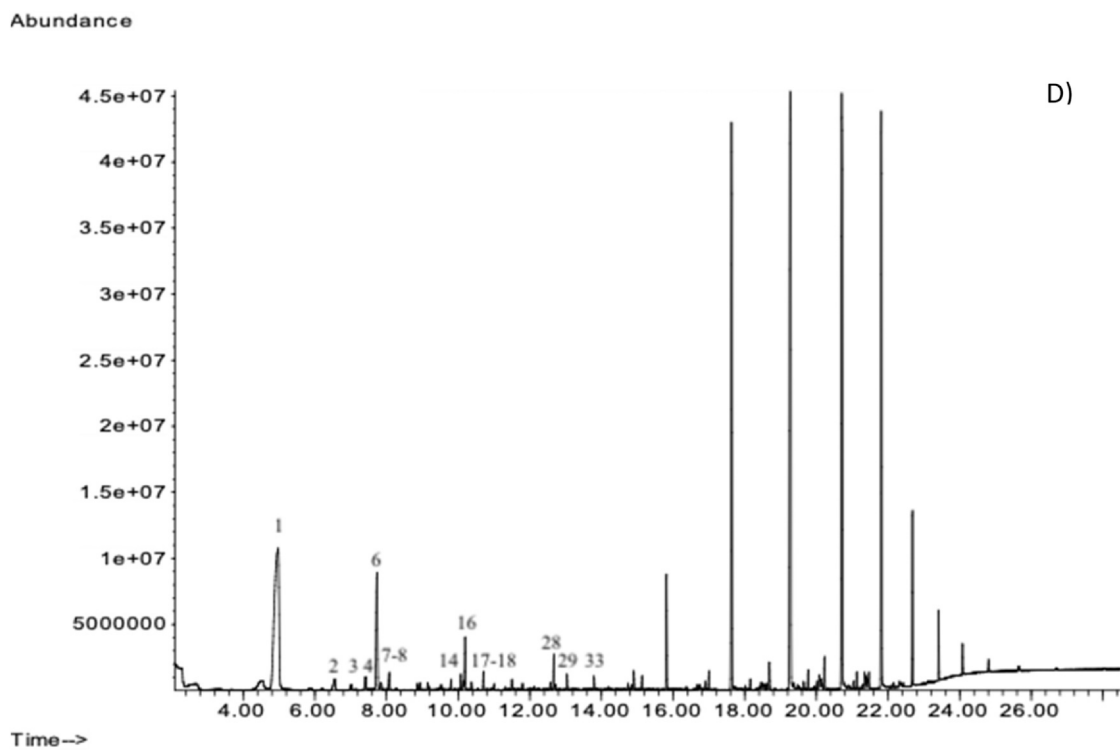
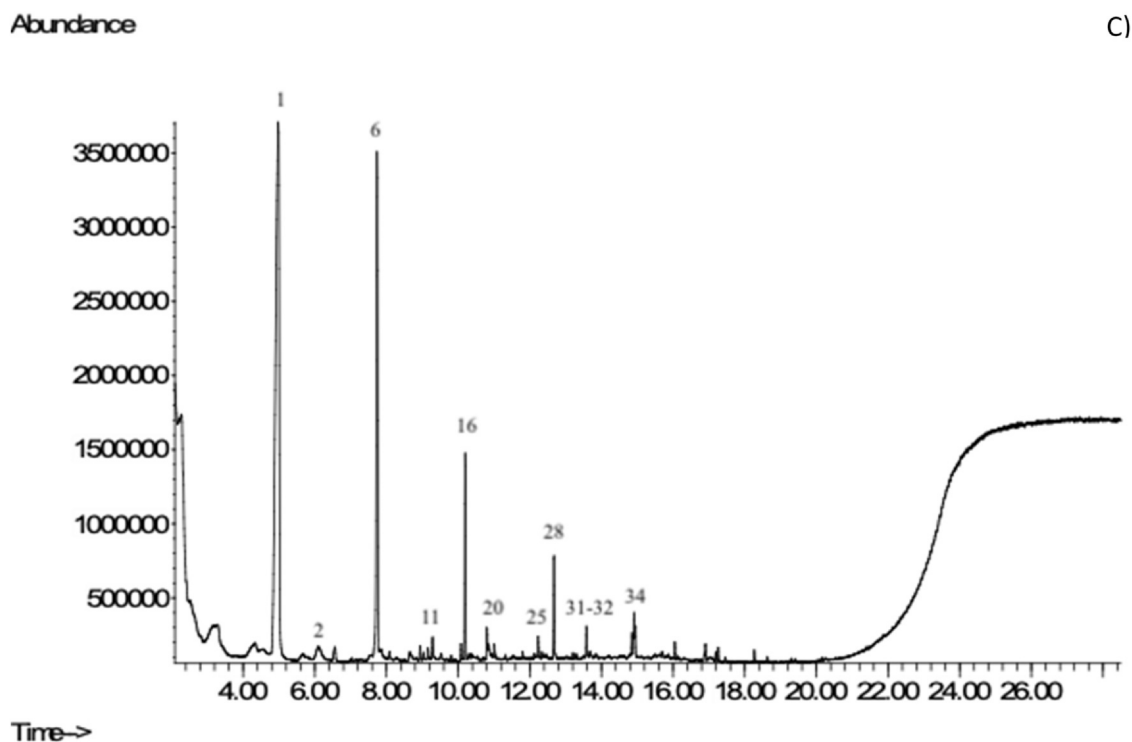


Fig. 3. (continued)

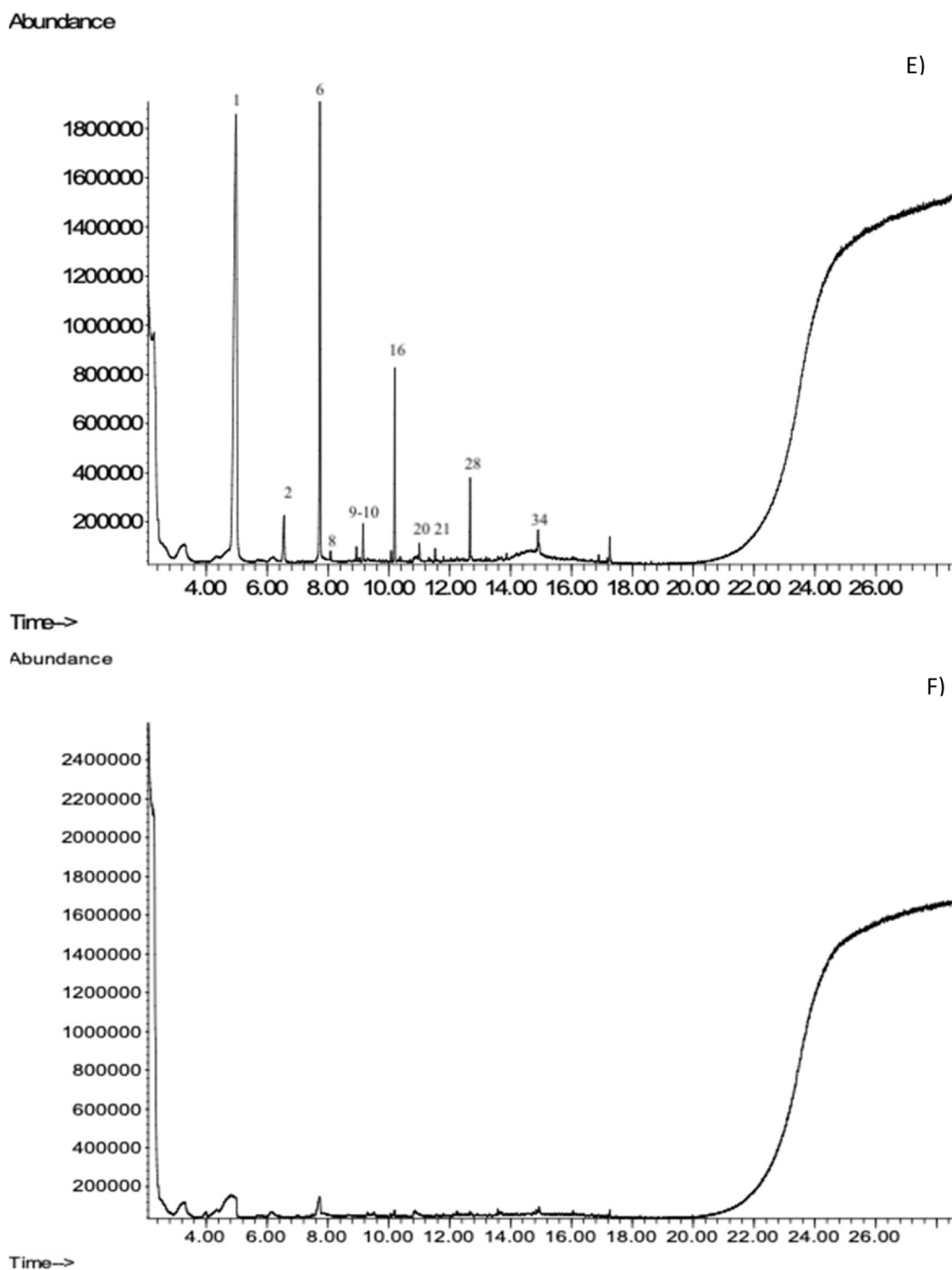


Fig. 3. (continued)

distribution of 9 additional peaks visually distinguished from the rest of the sample set. These peaks are not present in Table 2 as they occurred in only one sample, and hence were not included. These peaks presented similar mass spectra and different retention time. Comparison of the mass spectra with the NIST database allow to assess they were long chain silicones: respectively hexa- (15.712 min), hepta- (17.632 min), octa- (19.270 min), nona- (20.712 min), deca- (21.810 min) and undeca- (22.683) siloxanes. This suggests that

silicones of different chain lengths, and therefore of different viscosities, were used for different products [30,31].

Since the silicone-containing condoms all resulted in indistinguishable pyrograms, regardless of brand or type, it may be assumed that minor compounds, such as flavours or dyes, were not extracted by hexane. This was expected, due to the polarity of these compounds, and indicates that a polar solvent extraction followed by conventional GC-MS analysis should be considered in order to

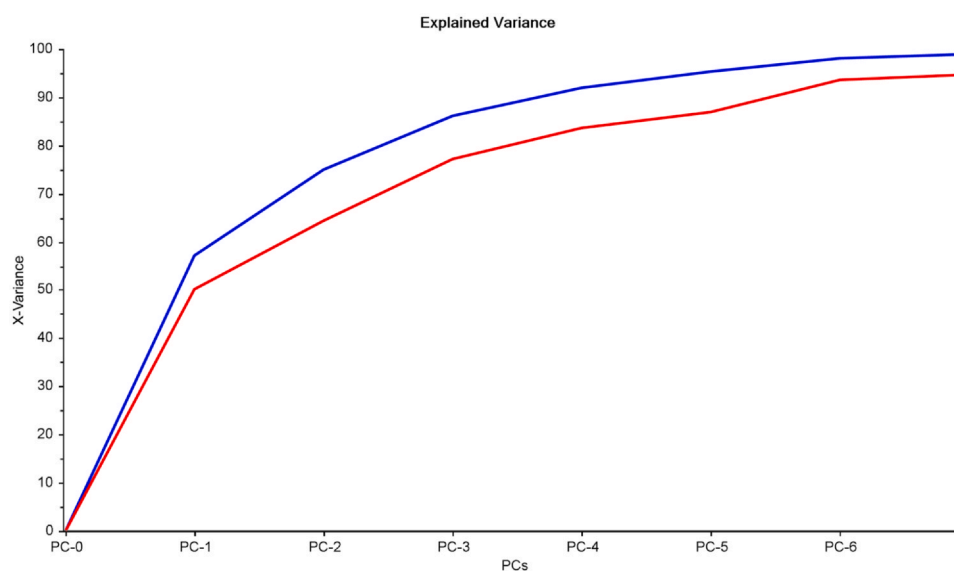


Fig. 4. Scree plot depicting the cumulative variance in the dataset retained by each PC. The red curve represents the first model with 50 PC and the blue curve the one with 10 PC. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

understand the exact composition of the sample. This may also further isolate compounds of interest for the discrimination of samples within classes. However, this must be handled with caution, as the likelihood of the transfer and persistence of these minor compounds is unknown, and they may potentially not be found in trace swabs.

Condoms are a mass-produced product in a regulated industry. Observations of visually indistinguishable profiles confirms the hypothesis that either very similar formulations are used by manufacturers or that all the PDMS used may come from one chemical manufacturer. Both hypotheses are possible as the number of PDMS suppliers around the world is unknown. Although DNA is the most common evidence to be collected from condoms, lubricants can also be used for both investigative and evaluative purposes. If no DNA is detected, the presence of a condom lubricant can infer the use of a condom and provide a possible explanation for the lack of any DNA. In these cases, the py-GC technique can answer questions of interest as the presence of diagnostic patterns from condom lubricants can infer the use of a condom and potentially the profile can be linked to one of the condom profiles in the database. The chemical profiles obtained from condoms were indistinguishable between condom manufacturers, and the chemical profiles obtained from personal lubricant were, in most cases, distinguishable from the condom ones. However, the initial target molecule was found to be the same, i.e. PDMS. Therefore, the hypothesis that the manufacturers use the same source of PDMS for condoms may be true. These observations also suggest that the PDMS used in lubricants is different to that used on condoms, in terms of viscosity and chain length, which results in the generation of different chemical profiles. Although pyrolysis is affected by the concentration of the sample [38,39], previous researches reported that higher viscosity lubricants produce more higher molecular weight cyclic oligomers (such as D9-D13) than lower viscosity lubricants [30,31]. In addition, it is known that peak area is linked to viscosity, the higher the viscosity, the higher the peak area of the cyclic oligomers, especially for the D3 oligomer [30]. This is a very interesting point to consider when it comes to a potential discrimination of the samples. The use of chemometrics and statistics was applied to evaluate the potential discrimination and classification of the samples constituting the dataset.

3.2. Sample discrimination

PCA was first performed on the entire dataset and considering all the 50 compounds listed in Table 2 after normalisation. Using 7 principal components explained up to 86% of the total variance of the dataset. After analysing the correlation of the variables using the loading plots, and considering the coefficient of variations for each compound as described by [33,40,41], a reduction of the variables set to 10 variables explained 99% of the variance of the dataset. Retained variables were D3, D4, D5, D6, linear D3, Unknown 7.02, Unknown 7.41, Unknown 7.86, linear D4 and Unknown 9.80.

Within this model, the first four principal components (PC) accounted for 94% of the total variance of the dataset, as illustrated by the scree plot (Fig. 4). Increasing the number of principal components up to 7 explained 99% of the variance of the dataset.

Fig. 5 shows the scores for the first 3 PCs (Fig. 5A) and for PC 1, 2 and 4 (Fig. 5B). Discrimination was not enhanced using supplementary principal components.

As illustrated in Fig. 5, condom samples were found to form two clusters: the first one from samples presenting the clear diagnostic pattern of siloxane degradation, and the second containing only 2 samples (FairSquared Sensitive Dry and Ceylor Gold) presenting unclear patterns of siloxane degradation, with significant variations of peak concentrations (see Fig. 3B). If FairSquared Sensitive Dry did not present any evidence of the presence of silicone compounds, Ceylor Gold presented a pattern different from the CH₃-PDMS (Fig. 6) but indistinguishable from OH-PDMS as illustrated in [42].

The pyrogram obtained from Ceylor Gold showed traces of cyclic oligomers (D3, D4 D5 and D6) in significantly lower amounts than what was previously observed for condom samples. A GC-MS analysis of polar compounds, extracted with methanol, detected a water-based lubricant (i.e. polyethylene glycol) and spermicide (i.e. nonoxynol-9) in the Ceylor Gold condom. FairSquared Sensitive Dry sample was difficult to analyse, as it is a dry condom. Dry condoms are usually not lubricated with classic lubricants (i.e. PDMS, Glycerol, PEG) but contain significant amounts of solid particles (e.g. polyethylene powder, cornstarch), which are not expected to be detected with the method presented here, as they are not extracted with hexane [37]. However, traces of cyclic oligomers D3-D6 were observed, in very low concentrations. No traces of solid particles, such

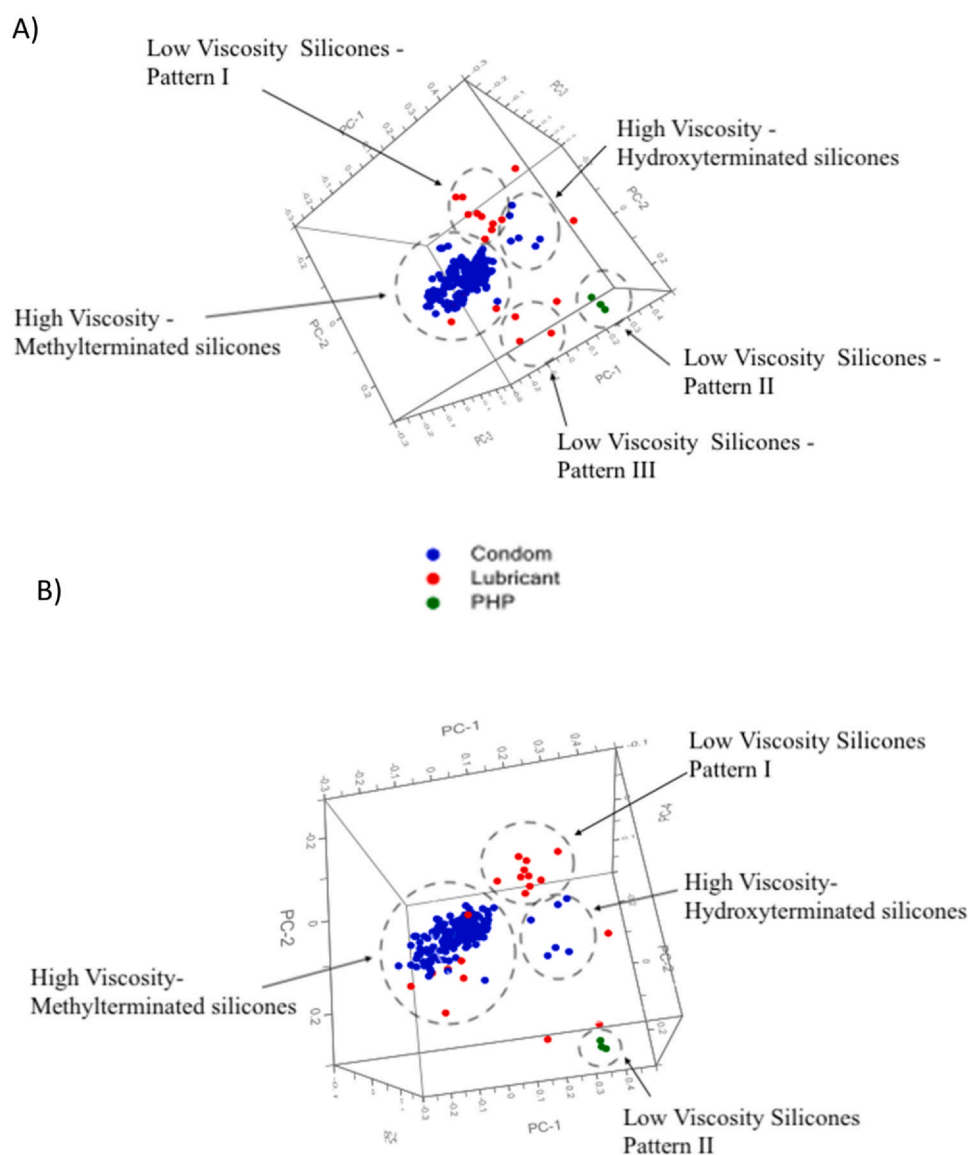


Fig. 5. 3-dimensional scores plot showing the distribution of the data collected from the 70 samples constituting the dataset. (A) Along PC1, PC2 and PC3, (B) along PC1, PC2 and PC4. In blue are the condoms, green the personal hygiene products and red the lubricants. Only one PHP sample is presented, as Sample 156-FemFresh Deodorant could not be properly analysed, due to solubilisation issues. Dotted circles indicate clusters assumed to represent a same population. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

as furfural, furaldehyde or furane derivatives, were found in the pyrolysis patterns. In the eventuality of the use of a dry condom in an alleged assault, stereomicroscopy and microscopy should be used to help detect these particles [2,24,43,44], as they are not being specifically extracted and/or detected using the hexane/Py-GC-MS protocol. These two samples are challenging, as their profiles might be misinterpreted as a “negative” profile when present in real world samples, given the low concentration of silicone lubricants. Hence, the absence of chemical residues should be carefully evaluated in the forensic context, with other techniques used to detect other types of compounds, or an evaluation of the factors affecting transfer and persistence of the samples in the matrix.

Within the cluster containing the majority of the condom samples, it was determined that one replicate from sample 40 (Durex Confidence) was slightly separated from the rest of the dataset, but not enough to be clustered with the other samples. It was found to be very close to lubricant sample 171 (Astroglide Diamond Silicone Gel Personal Lubricant). This replicate can be considered an outlier,

possibly due to a cross contamination and was removed from classification models using the classification algorithm. Replicates from sample 64 (Lifestyles Assorted Choc Ripple Ribbed) were found to be slightly separated from the major condom group, as their scores along PC1, 2 and 3 were observably different. Two replicates presented a positive value along PC1, whereas the rest of the condoms were found to have negative values along this PC. Similarly, values along PC2 for most condoms were around 0.002 and was over 0.1 for sample 64. The PC3 value for sample 64 was negative, whereas all other condoms had positive values. As the pyrogram for sample 64 was visually similar to all the other condoms, flavourings were not considered as the source of the observed classification difference. A possible hypothesis is that changes in the structure of the latex (i.e. ribbed condoms) generated variations in the amount of lubricant that can be added, resulting in this condom being distinguished from the rest of the sample set. However, the other ribbed condom present (sample 184 – Ansell LifeStyles Ribbed Condoms) was not found to be distinguished from the rest of the dataset.

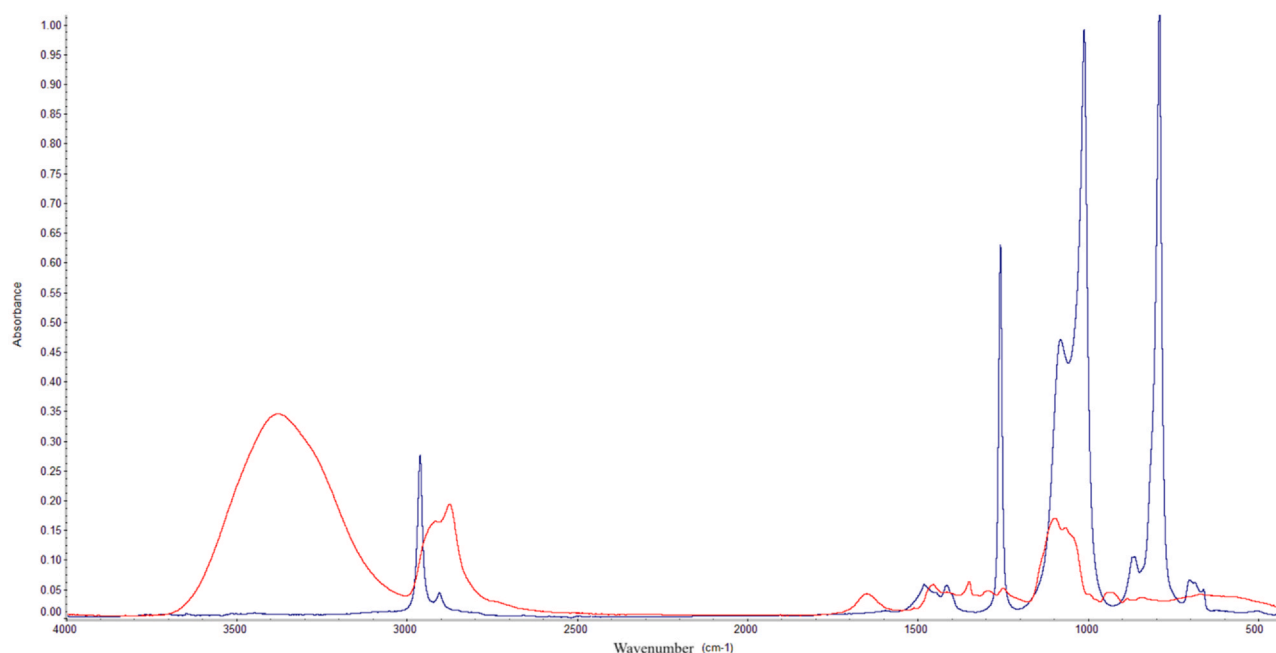


Fig. 6. ATR-FTIR spectra of Ceylor Gold sample (in red), and a silicone-based sample (in blue) for comparison. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Therefore, except for condoms presenting visual distinguishable patterns, it was not possible to differentiate silicone-based lubricated condoms.

Lubricants initially presented several visually different patterns. The statistical model confirmed that it was possible to differentiate the samples, mainly into 3 groups. One lubricant, sample 181 (Durex Perfect Play Glide), was found to cluster with condom samples, and could not be separated with subsequent PCs. When examining the chemical profile, there was no difference noted between this profile and the ones coming from the condoms. It was the only lubricant that was classified with condom samples. Sample 171 (Astroglide Diamond Silicone Gel Personal Lubricant) was found to separate to an isolated cluster, close to the condom samples. However, PC2 and PC4 helped separate this sample from the condom sample set. As the chemical profiles obtained for lubricants were differentiated, visually, statistically and semi-quantitatively, it can therefore be concluded that in general, the chemical profiles of condoms differ from those of lubricants, although in both types a silicone composition is observed. This suggests that silicones of different chain lengths, and therefore different viscosities, are used for different products.

Three outliers from the groupings were noted, which were replicate 2 from sample 172 (Astroglide Gel Personal Lubricant), replicate 3 from sample 109 (Ansell LifeStyles Luxe Silicone-based Lubricant) and replicate 2 from sample 168 (Ansell Skyn Intimate Moments). These replicates were significantly spread and plotted away from the other replicates of the same samples, thus indicating that there may have been some variation, either at the acquisition of the chromatogram or during the extraction of the data procedure. These samples were not considered in the classification steps. Regarding sample 172, the pattern of silicone peaks was close to the background and hence, may not be detected in casework. In addition, sample 172 was a water-based lubricant, thus GC-MS analysis may be more appropriate for analysis and interpretation than py-GC-MS [45]. Therefore, it was removed from the sample set when performing the classification process.

The smallest class of the dataset, personal hygiene products, was under-represented in this model. Indeed, only one of the 70 samples available in the initial dataset presented a silicone-based chemical profile when analysed with a screening method, such as FTIR [25].

The chemical profile obtained for this sample 156 (FemFresh Intimate Deodorant) was inconclusive, resulting in it being clustered significantly separately to the rest of the dataset. Replicates showed a higher variability than for the rest of the dataset, and the detection of silicones was found to be inconsistent between analyses. This might be due to its aerosol nature, which made it quite challenging to collect sufficient residues for analysis. However, from the chemical and statistical point of view, the residues from this sample were found to be distinguishable from the rest of the dataset.

Finally, all seventy samples constituting the dataset were grouped into five categories that were observed on the overall dataset using both qualitative and statistical analyses, the lists of which are presented in Table 3. Results gathered from Table 3 shows that 85.7% of the silicone profiles observed are belonging to Group 1, 7.14% to Group 2, 2.86% to Group 3, 1.43% to Group 4% and 2.86% to Group 5. 96.72% of condom present a Group 1 profile, and the left-over condoms present a Group 3 profile. Amongst the lubricant population, 14.28% presented a Group 1 profile, 71.42% a Group 2 profile, 14.28% a Group 4 profile. Group 5 was exclusively made of personal hygiene products.

The discriminating power of the method was calculated, and was found to be 0.26 for the overall groupings. This is not really high, but is not surprising either, firstly because condoms are overrepresented in the dataset, and secondly because ISO norms regulations on condom manufacturing make it harder to find different chemical profile in a condom population. The discrimination of the samples

Table 3

Summary of the sample(s) comprised in each grouping, considering that all samples were containing silicones.

Group	Source of the sample	Samples in the group
Group 1	Condom (59) Lubricants (1)	Samples 1, 10, 11, 12, 13, 14, 20, 23, 24, 33, 34, 36, 38, 40–50, 53–56, 58–66, 68, 69, 79, 110–115, 117–123, 125–127, 130, 178–184
Group 2	Lubricants (5)	Samples 109, 133, 168, 172, 174
Group 3	Condom (2)	Samples 116, 124
Group 4	Lubricants (1)	Sample 171
Group 5	PHP (2)	Sample 156, 158

Table 4

Confusion matrix for discriminant analysis applied on the entire dataset, constituted of the replicates of the 68 samples, classification based on the class using QDA algorithm.

QDA	Condom	Lubricant
Condom	169	1
Lubricant	4	16

contained in Group 1 could probably be enhanced by the use of other instrumentations, such as DART-MS as described by Baumgarten et al. [9], but such a choice should be dictated by the question targeted by the forensic scientist.

3.3. Classification model

Replicates of the seventy samples were classified according to the class to which they belonged. However, considering that the personal hygiene product class contained only 2 samples clearly distinguished from the rest of the dataset, they were removed from the classification model. Thus, the samples were grouped into two categories. The quadratic discriminant analysis was applied to the scores of the first four principal components, since these were necessary for the separation of the samples, using 2/3 of the dataset as the training set and 1/3 of the dataset as the validation set. A good classification rate of 97.37% was obtained. The confusion matrix is presented in Table 4.

The misclassified replicates were evaluated. One replicate of Sample 40 (Durex Confidence) was classified in the lubricant category. The PCA results indicated a very close proximity between the chemical profile of this replicate and that of sample 171. The replicate of sample 40 that misclassified was the closest to the replicates of sample 171.

Two replicates of sample 64 (Ansell Lifestyles - Assorted - Choc Ripple Ribbed) were classified in the lubricant category instead of the condom category. These samples were not outliers. The results of the PCA showed that the chemical profiles of these condoms were slightly separated from the condom population to which they were expected to belong, although it was not possible to assign them to another class. The centroid of the condom group was found to be located around 0.005 along PC1 and -0.018 along PC2, whereas the lubricant group was located around 0.17 along PC1 and -0.06 along PC2. Classification values obtained for the two replicates were found to be negative for clustering to the condom group and were found to be positive for clustering with the lubricant group, the distance being 0.05 to the condom group, and 0.11 to the lubricant group for the first replicate, and 0.04 and 0.12 for the second. The third replicate presented eigenvalues of -0.007 and 0.03 along PC1 and PC2, making this sample closely clustered with the condom class. Given the difference in coefficient of distance to the centroid, this suggests that an additional class should be suspected. As previously stated, such a class could be due to changes in the structure of the latex (i.e. ribbed condoms), which would generate variations in the amount of lubricant that can be added to it, thus they could be distinguished from the rest of the sample set. This hypothesis is also suggested as it is known that pyrolysis is sensitive to the amount of sample deposited in the cup, as illustrated by previous publications [23,32,33,46]. Therefore, a difference in the concentration is likely to generate a difference in the amount of sample in the cup after evaporation and thus affect the chemical profile.

A replicate of Sample 60 (Ansell Lifestyles - Assorted - Banana Bump Studded) was classified into the lubricant category, instead of the condom category. Visual examination of the chemical profile did not allow it to be distinguished from the rest of the condom population. The results of the PCA showed that the chemical profile of this condom was slightly separated from the condom population to

which it was expected to belong. However, the other 2 replicates were clustered appropriately within the condom population. These observations correspond to the previous ribbed sample that also had classification issues, reinforcing the hypothesis that changes in the structure of the latex (i.e. ribbed condoms), would generate variations in the amount of lubricant and therefore in the discrimination and classification patterns.

One replicate of Sample 168 (Ansell Skyn Intimate Moments) was classified in the condom category, instead of the lubricant category. The PCA results indicated proximity between the chemical profile of this replicate and that of the condom population. The classification results are thus compatible with what was observed for the PCA, and it was not surprising that the classification model was not able to correctly classify this sample.

The three replicates of sample 181 (Durex Perfect Play Glide), which presented a chemical profile different to the condom ones, were correctly classified in the lubricant category. Visual analysis and observation of the PCA scores plot indicated that the chemical profile of this silicone-based lubricant was indistinguishable to the chemical profiles obtained for condom-type samples. However, the QDA algorithm correctly clustered these samples in the lubricant classes. Evaluation of the eigenvalues showed out that the separation was led along PC4, with the condom groups presenting an average value of 0.00029 and the lubricants one of 0.023. The sample eigenvalue was 0.04 (± 0.01) which makes it cluster to the lubricants class. This is surprising, since it would have been reasonable to expect these samples to be misclassified. The algorithm was able to differentiate samples that were very close during the analysis by principal component, however this may not be the case when additional samples are added to the dataset. In addition, the distance between this sample and the centroid of the lubricant samples is smaller than the distance between the sample and the centroid of the condom samples, which is not surprising considering the variability coming out of the condom cluster. These observations reveal that QDA is reinforcing the quality of the classification procedure, as visual analysis of the data, or investigation of the eigenvalues might not be sufficient to classify the samples in the correct classes.

The results previously discussed show that the quadratic discriminant analysis provided results corresponding to what had been observed for PCA. Most false classifications were one of the replicates of a sample having slightly variable characteristics, leading to a correlation to samples within the population of another class. The study of misclassifications, supported by the results of the PCA, indicates that these samples generally differ not in terms of their visual chemical profile but in semi-quantitative terms. These differences can generally be explained by analytical and operator variations, such as spiking reproducibility or manual integration of the peaks, especially considering the great variability that occurs in pyrolysis events. Variations in the quantitative amounts present in the various samples may also explain the observed variations, although the chemical profiles do not differ significantly.

The classification model based on classes of silicone-based samples can thus be validly used to predict the class (i.e. condom or lubricant) of a trace whose origin is unknown. Two limitations to the use of this model can be encountered. The main limitation is that the detection of the fifty peaks used to build the model may not be present in real cases, since the interaction with the vaginal matrix has not, at present, been fully examined. A focus on the major cyclic oligomers is recommended, and this is the reason why the presented model was built only with 10 out of 50 compounds. The second limitation is that, the proportion of lubricants and intimate hygiene products based on silicones is relatively low and consequently, it is possible that other samples present on the market may contain different chemical profiles. On the opposite, the condom population included different brands and types, flavoured and coloured

samples, those containing specific additives, with or without latex and a range of prices to be the most representative. However, a comprehensive model may not be feasible, the number of brands and types on the market being relatively large (more than 200 products on the Swiss market, and almost as many on the Australian market). In addition, new products are frequently released on the market and hence a continuous update of the model may prove necessary, although the list of authorised lubricants is not constantly changing.

The discriminant analysis models were used to assess the possibility of statistically differentiating the samples from the dataset, based on their chemical profiles. The main conclusion from these models is that condoms of different brands and types, the lubricant of which is based on silicones, are generally not differentiable. Samples of different classes that do not differ qualitatively can be differentiated. Samples of different sources (condom, lubricants, PHP) that show slight differences in the level of minor compounds can generally be differentiated, but only if these compounds are detected. Application to casework revealed that these minor compounds were also observed when trace evidence was analysed. When considering a possible use to courtroom, the forensic expert could either use the classification scheme with reported error rates or choose to use a Bayesian approach to provide the court with a likelihood ratio on the source level. Examples of classification using Bayesian framework are presented in many different areas of forensic sciences and could easily be derived for an application to condom evidence [47–49]. However, further research are required regarding other pending questions such as background, transfer and

persistence of the evidence in a vaginal matrix, so as to be able to provide the Court a more adequate information on the observed evidence.

3.4. Investigation of brand discrimination

Although the results of the qualitative analysis did not reveal any profiles specific to a type of condom or to a brand, it was of interest to investigate potential brand discriminations. The results of the PCA did not reveal any features that would allow separation by brand or type (Fig. 7). The chemical profiles of different condoms do not differ significantly between brands, nor do the chemical profiles of condoms of different types within the same brand. These findings indicate that the variation between the different condom manufacturers is very small. This is likely due to the very high level of control and international regulations for the production of condoms and limited PDMS suppliers [14–17].

Under these conditions, the classification model has 14 categories. LDA and QDA were not attempted as some classes contained too few samples for reliable modelling. The classification performed with an SVM model gave a classification rate of 54.74%, with 51.05% for cross validation. The classification rate was not satisfactory, but this was not surprising in view of the observations highlighted during the PCA. Multiple other discriminations were investigated, such as the purchasing location, whether different models coming from a same brand were different, or even if same brand, same model and different production could be distinguished, but none of these were successful.

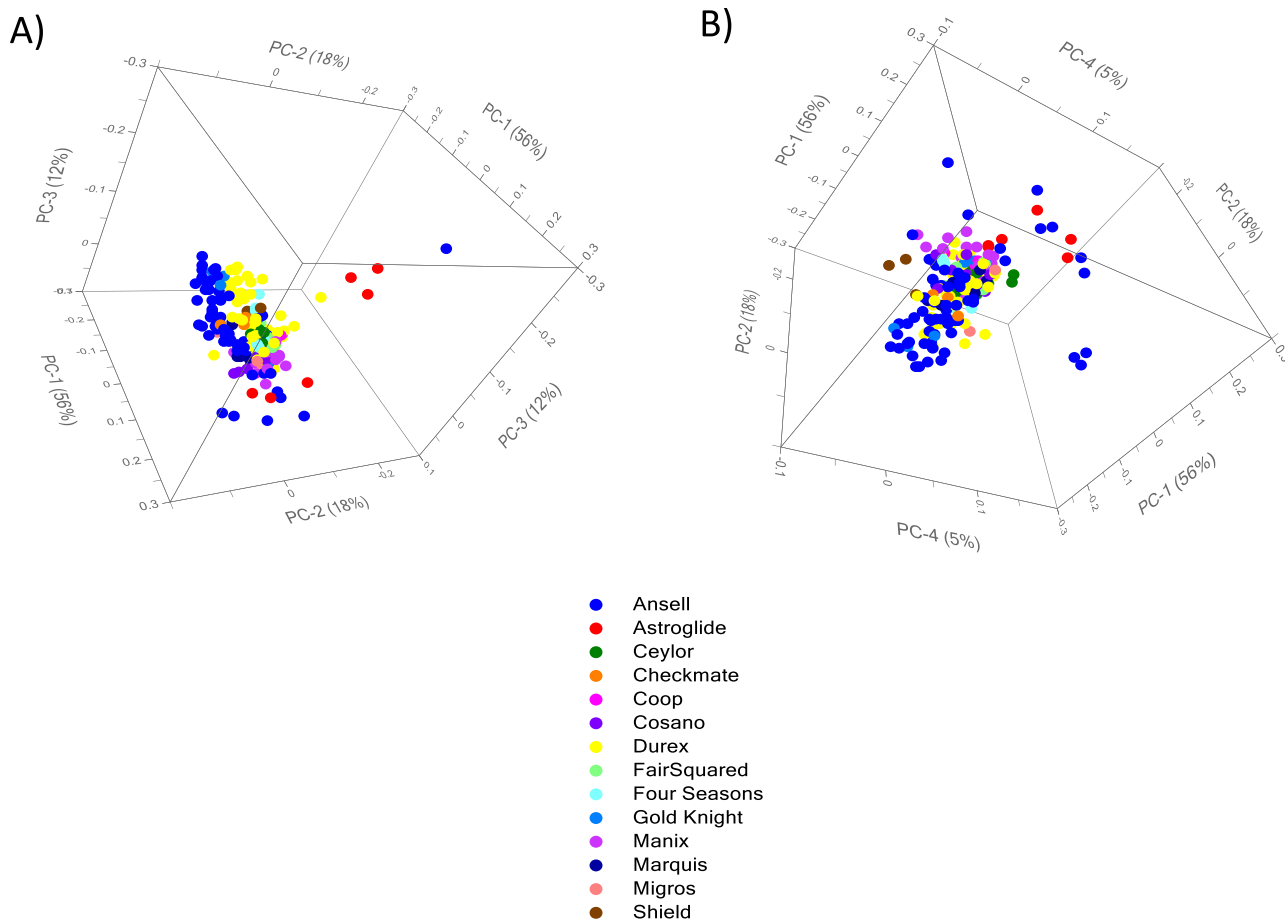


Fig. 7. 3-dimensional scores plot showing the distribution of the data collected from the 70 samples constituting the dataset. (A) Along PC1, PC2 and PC3, (B) along PC1, PC2 and PC4. Classification based on the brand.

4. Conclusion

In this study, 70 samples consisting of condoms, lubricants and personal hygiene products containing silicone, and purchased on 3 different markets, were analysed to evaluate the potential discrimination of these samples. To achieve this goal, py-GC-MS was used as it is known to be able to detect siloxanes with good sensitivity. Based on chemical compositions, at least 6 different groups were observed, and it was found that some lubricants were belonging to the same group than condom, due to similarities in compositions.

Chemical profiles were found to be repeatable with good resolution obtained in all the pyrograms. Upon visual examination, pyrograms were dominated by cyclic oligomers resulting from the degradation of PDMS, but another 40 compounds were also detected, without being linked to any specific molecule. Only 10 out of 50 compounds were necessary to obtain a good discrimination, the rest of it not allowing to enhance sample separation in the dataset. No traces of aroma, flavourings, colourants or water-based residues were detected in the pyrograms of the samples, highlighting the need for complementary methods, such as GC/MS or ATR-FTIR, if these compounds are of interest.

This study confirms that pyrolysis GC-MS is one of the most suitable techniques for PDMS lubricant analysis. However, it does not solve the question of water-based lubricated condoms and non-lubricated condoms, outlining the need for further research for these sample types. The methodology was found to be applicable in casework situation. Future research is needed to investigate transfer interaction with the vaginal matrix, and other persistence factors to evaluate full applicability to casework, including relevant interpretation of the evidence. This will provide a baseline to implement this analysis in real world cases.

CRedit authorship contribution statement

Céline Burnier: Writing - original draft. **Geneviève Massonnet, Sally Coulson, Kari Pitts, David DeTata :** Writing/Reviewing. **Kari Pitts, David DeTata, Sally Coulson:** Conceptualization. **Céline Burnier, Kari Pitts, David DeTata:** Methodology. **Céline Burnier:** Validation, Investigation, Data curation, Visualization. **Kari Pitts, David DeTata, Sally Coulson:** Resources. **Kari Pitts, David DeTata:** Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors would like to acknowledge Curtin Institute for Functional Molecules and Imaging (Curtin University, Australia) for providing funds for sample collection, Prof. Simon Lewis and Dr Georgina Sauzier for assistance in data processing, and MSc. Valentina Cammarotta from the School of Criminal Justice for the assistance on the interpretation of the evidence.

Funding

This research was partially funded by Fondation pour l'Université de Lausanne (Lausanne, Switzerland), who covered travel grants.

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.forsciint.2021.110793](https://doi.org/10.1016/j.forsciint.2021.110793).

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