

## Microfurnace or filament pyrolyzer: an example of pyrolysis-GC/MS for condom lubricant analysis

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### ABSTRACT

Condom lubricants have been shown to contain polydimethylsiloxane (PDMS) in over 95% of cases, but PDMS is difficult to analyze using standard GC-MS or LC-MS due to their size, apolarity and issues with solvents and plasticizers. Py-GC-MS was established as one of the more relevant analytical techniques for PDMS evidence analysis. However, different pyrolysis units and various GC columns are available for use Py-GC-MS. These two parameters are likely to significantly affect the repeatability, reproducibility and sensitivity of the analysis and, as such, affect the recovery of condom traces in casework. This work employed a resistively heated filament pyrolyzer and an isothermal oven pyrolyzer to investigate differences in the profiles generated by the pyrolysis units in the analysis of 4 condom lubricants. Similar experiments were performed using different columns, with the same pyrolyzers, to determine which gave optimal compound separation. This enabled assessment of the combinations in terms of the qualitative and semi-quantitative repeatability, allowing recommendations for optimized condom residue analysis. Results indicate that the use of a HP-5MS column, coupled to an isothermal oven pyrolyzer, is the optimal instrument configuration for condom residue analysis, based on repeatability, reproducibility and sensitivity of PDMS analysis.

### Introduction

Sexual assaults are a pervasive problem in our society, considered in our judicial system as especially serious.<sup>1</sup> In a sexual assault investigation, the first forensic trace that is usually sought is DNA, in addition to the victim's medical examination findings. However, in many cases, the perpetrator may use a condom to limit transfer of biological traces and the chances of recovering a perpetrator's DNA from the victim are significantly reduced. Currently, complementary evidence in addition to DNA is required to be able to proceed. The best illustration is the Farah Jama case in Australia: DNA was used as the sole evidence of sexual assault, resulting in the wrongful conviction of the supposed perpetrator. The circumstances leading to this error were investigated, resulting in the Vincent Report, a text stipulating that no case should proceed on DNA evidence alone without specific sign off by the Attorney General [1]. For these reasons, condom evidence is pivotal to the

reconstruction and successful prosecution of sexual assault cases. However, there is a lack of research in this area that may equally lead to wrongful convictions, such as in the Malkinson case. In this case, a silicone trace was attributed to a condom when there was no existing model available to reliably assess this evidence [2]. Cases reported in the literature [3–5] show that the analysis and interpretation of traces of condoms is a significant challenge worldwide [6–11].

A quick overview of the literature highlights significant developments in the area of condom evidence since 2016. Silicone lubricants, more specifically polydimethylsiloxane (PDMS) [4,5,12–15], are detectable in 95% of cases involving condom residue transfer during intercourse [12,13,16,17,5,7], while glycerine, propylene and/or ethylene glycol can also be detected [18–20]. In a case study published in 2021 [6] the authors illustrate the use of an analytical sequence consisting of infrared spectroscopy and gas chromatography. Classic gas chromatography does not allow the analysis of silicone lubricants due to

*Abbreviations:* CV%, Coefficient of variation in percent; GC, Gas Chromatography; PDMS, Polydimethylsiloxane; py-GC/MS, Pyrolysis gas chromatography mass spectrometry; RRT, Relative retention time.

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<sup>1</sup> <https://www.unfpa.org/gender-based-violence>.

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their size and lack of volatility. Therefore, studies were performed on the use of pyrolysis coupled to gas chromatography for the analysis of silicone lubricants [10,17,21–23]. Amongst other factors, these studies report pyrolysis parameters [21] and discrimination of various condom brands and models [22], while using two different types of pyrolysis units: filament and microfurnace. An underlying consideration here is which unit is the most suitable for this type of analysis. A similar question arises when reviewing the GC columns used in the different papers, which may be apolar or mid-polar.

The aim of the present paper is to compare the performances of different types of pyrolysis units and columns to help practitioners decide which to use in their routine practice. Each device was used for sample analysis with the same column type (i.e. HP-5MS) to examine instrument response. Further studies on two different columns were used on the same instrument (Frontier Lab. py-3030S) to evaluate the quality of the separation as a function of column polarity.

## Material & methods

### Instrumentation

The two different pyrolysis devices used are described hereafter. The pyrolysis temperature was set at 720 °C, according to literature [21,22]. All parameters were selected for the detection of polydimethylsiloxane, the most common condom lubricant found on the market [4,5,12–15].

#### Instrument 1 – filament pyrolyzer

A resistively heated filament Pyroprobe 5150 from CDS Analytical Inc was coupled to an Agilent 6890 N GC system interfaced with an Agilent 5975C mass spectrometry detector. Software used were respectively Pyroprobe 3.21 from CDS and ChemStation v. D00.01.27 from Agilent.

The analytical procedure was based on previous research on optimization of py-GC/MS parameters for silicone analysis [21]. 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 set at 280 °C. The temperature program was as follows: 50 °C for 2 min, 10 °C/min to 230 °C, 20 °C/min to 300 °C, and hold 5 min at 300 °C. For mass spectrometry 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.

#### Instrument 2 – furnace pyrolyzer

The second instrument was an isothermal oven Frontier Lab. py-3030S single shot pyrolyzer device coupled to an Agilent GC 7890B system, interfaced with an Agilent 5977 N mass spectrometry detector. Softwares used were respectively Py3030S Control (v. 1.77) from Frontier Laboratories and ChemStation v. F.01.03.2357 from Agilent.

This instrument was used for the column investigation, using a HP-5MS capillary column (30 m x 0.25 mm x 0.25 µm) as the apolar column and a DB1701 capillary column (30 m x 0.25 mm x 0.25 µm) as the mid-polar column. Helium was used as a carrier gas at a flow rate of 1 mL/min, with injections carried out in splitless mode and an injector temperature of 280 °C. The chromatographic program for the HP5-MS column was identical to the one used for the CDS Analytical instrument. The maximal temperature of the DB1701 column was 280 °C, therefore chromatographic parameters were: 50 °C for 2 min, 10 °C/min to 230 °C, 20 °C/min to 280 °C, and hold 5 min at 280 °C. Mass spectrometry detection parameters were as set for the CDS Analytical instrument.

### Samples and preparation

Analytical grade hexane (Sigma Aldrich, USA) was used as received. Quartz pyrolysis tubes and glass wool were obtained from CDS

Analytical (USA). A 5 µl eVol XR ® syringe was purchased from SGE (Trajan) and Eco-Cup SF and Eco-Sticks SF from Frontier Laboratories. Five different condom samples were taken from a selection of silicone lubricated condoms identified by Burnier et al. (2021) [22]. The condoms were from the major brands on the market and with different composition, including presence of lidocaine/benzocaine and flavorings. Table 1 resumes the properties of the selected condoms.

Sample preparation was based on published procedures [6,7,9–11,13,17,22]. Condom samples were opened, unrolled, placed in a 100 mL glass bottle, and covered with 50 mL of hexane. The bottles were then closed and ultrasonicated for 15 min. Before analysis, samples were aliquoted and diluted tenfold with hexane. For samples analyzed with the CDS Analytical instrument, 3 µL aliquots of the solution were spiked into the quartz tube on glass wool and left to evaporate before analysis. For samples analyzed with the Frontier Pyrolysis instrument, 10 µL of the solution were spiked in the same manner. The differences in sample aliquots are based on optimization parameters as described in the literature [7,13,17,21,22]. Each sample was analyzed five times to account for instrumental variation.

### Methodology

Data analysis was performed using Agilent Technologies' Enhanced Data Analysis MSD ChemStation software (v. D.02.00.275). Chromatograms were overlaid to visualize the repeatability within each sample. The presence or absence of peaks, the number of peaks, their position (relative retention time), the patterns created, and relative abundance were observed. All the various compounds present in each chromatogram were then characterized using NIST18, TOX, and Wiley databases and literature [17,23–26]. Only compounds with peak heights of over 10,000 AU were considered. Matching criteria were based on presence of qualifier, their relative abundance, and visual pattern.

17 pyrolysis compounds were selected for the semi-quantitative analysis (Table 2, Fig. 1). Target ion and qualifiers were selected based on existing literature [17,22]. The choice was based on three criteria:

1. They are abundant enough and well resolved;
2. They are diagnostics of the silicone (more specifically PDMS) pattern, as presented in the literature [17,21–23];
3. They are present in all chromatograms acquired with the different instruments.

Statistical processing was carried out using R software (v. 1.2.1335). Data were normalized according to an existing procedure [21]: peak area of the target compounds were normalized to total areausum followed by double square root processing. The mean, standard deviation, and coefficient of variation were calculated for each compound. Coefficient of variation acceptance criteria was set at 10% [21,22,27,28]. Statistical comparisons of relative areas were processed using Student's T- test with a 95% confidence interval.

**Table 1**  
Selected condoms and their properties.

Condom	Lubricant	Flavorings	Anaesthetics	Support
Durex Natural	PDMS	–	–	Latex
Ceylor Blue	–	–	–	Latex
Manix Skyn	–	–	–	Latex free
Manix Strawberry	–	yes	–	Latex
Manix Orgazmax	–	–	yes	Latex

**Table 2**

Compounds selected to compare the results obtained with the CDS Analytical instrument and the Frontier Lab. instrument.

PEAK N°	RRT (MIN)	COMPOUND NAME	TARGET ION (M/Z)	QUALIFIERS (M/Z)
1	0	D3	207	191, 133, 96
2	1.53	Unknown 5.9	207	192, 221, 176
3	1.985	Unknown 6.4	192	208, 96, 135
4	2.38	Unknown 6.8	207	223, 190, 133
5	2.695	D4	281	265, 193, 133
6	2.805	Unknown 7.2	266	126, 250, 192
7	3.88	Acridine orange	264	248, 190, 125
8	4.475	Unknown 8.8	266	248, 190, 125
9	4.755	Unknown 9.1	341	324, 163, 73
10	5.02	Unknown 9.4	341	334, 162, 73
11	5.14	D5	355	266, 73
12	6.745	Unknown 11.7	326	415, 73, 398
13	7.61	D6	341	429, 324, 147
14	9.845	D7	281	503, 415, 147
15	11.845	D8	355	401, 281, 221
16	13.575	D9	429	236, 196, 146
17	15.115	D10	503	146, 280, 355

## Results & discussion

### Preliminary considerations

Regarding sample extraction, the most straightforward approach would have been to scrape the lubricants off the condom and introduce them directly in the pyrolyzer. However, the method employed in this study was chosen as the most common way to access condom residues in casework, with particular consideration to cotton swabs collected from victims [6,9–11,17]. With an aim to assist practitioners, extracting samples through a procedure more representative of casework was considered to be the best option here.

The liquid sample extract presented slightly more difficulties with the filament pyrolyzer compared to the furnace pyrolyzer: the use of an open-ended quartz tube, which was then placed vertically into the filament, resulted in leaks and loss of sample. To limit this, samples were spiked into horizontal tubes and left to dry before being placed into the filament. From a practical point of view, the use of a furnace pyrolyzer with stainless steel cups is a more effective approach.

In terms of analytical parameters, the temperature of pyrolysis was based on existing research, which indicated an optimal pyrolysis temperature of 720 °C. Confirmation of the best temperature between 620 °C and 720 °C was performed prior to running any analysis, but will not be presented here.

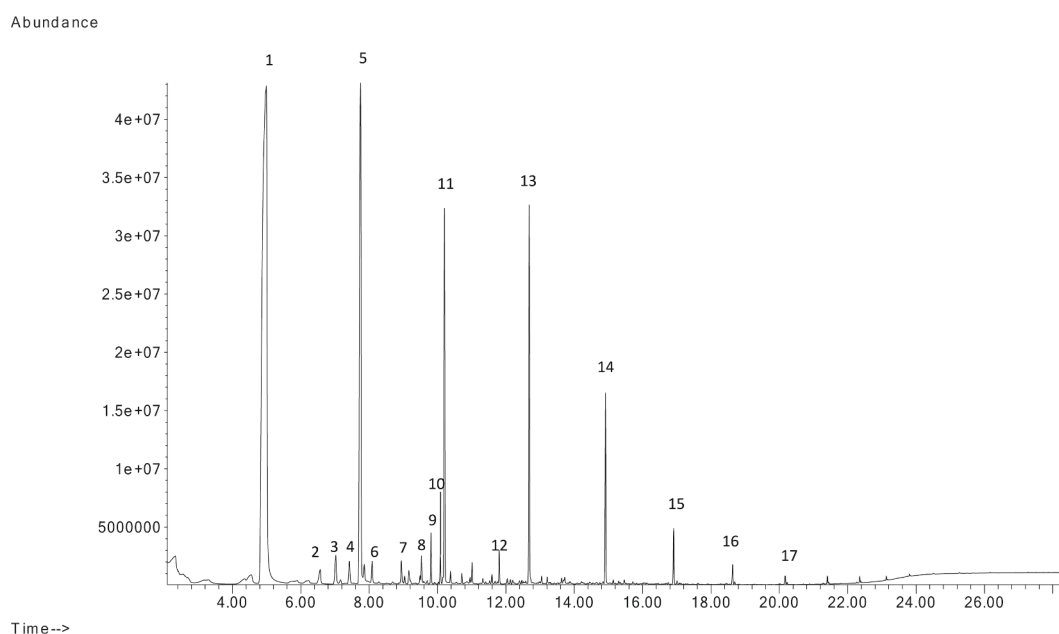
There is a debate surrounding whether increasing the total flow could lead to decreased by-product formation due to shorter sample residence times within the pyrolysis chamber. Some advocate for employing a split flow configuration to achieve this goal. However, the practicality of this approach is hindered by the low concentrations of silicones typically found in casework samples. Even with splitless injection, only the D3 oligomer is visible, and its detection within vaginal and swab matrices is challenging [6]. Furthermore, in our study, the filament pyrolyzer utilized a transfer line maintained at 300 °C, which is notably lower than the pyrolysis temperature. The extended length of the transfer line presents opportunities for recombination and condensation of by-products. Conversely, the furnace pyrolyzer directly positioned above the GC injector significantly reduces by-product formation. Therefore, while employing a split flow might mitigate the by-product challenge, utilizing a splitless mode coupled with a 1 ml/min carrier gas flow rate ensures that the entire sample remains within the GC column, thus enhancing the detection of trace-level products [29].

All pyrograms obtained presented the expected range of oligomers from the degradation of polydimethylsiloxane (PDMS) observed on PDMS 200cSt purchased from Sigma Aldrich [7,17,23]. These compounds were used as known reference points to evaluate and identify minor components in the different pyrograms. These reference points are essential because the use of various columns induces variations in the retention time of peaks. Therefore, relative retention times relative to the D3 peak (RRT), were used to compare the position of the peaks of interest.

### Impact of the pyrolysis device

#### Qualitative analysis

For the furnace pyrolysis, the overlay of the replicate pyrograms of each sample showed good visual repeatability in terms of peak presence/absence, numbers of peaks, and retention times between the D3 oligomer (RT between 4.00 and 5.00 min) and 23.00 min (Fig. 2). No



**Fig. 1.** Typical chromatographic pattern of reference PDMS, 200cSt viscosity, acquired on an isothermal oven Frontier Lab. py-3030S single shot pyrolyzer device coupled to an Agilent GC 7890B system. Compounds were selected for the extraction macro. Compounds numbers are related to Table 2.

further peaks were detected after 23.00 min. Differences were observed in the non-repeatable presence of one poorly resolved peak, prior to the D3 oligomer, in the pyrograms obtained with the furnace pyrolyzer. This peak was identified as hexan-2,5-dione. The presence of this peak is due to incomplete evaporation of the solvent prior to analysis [22].

Results obtained with the filament pyrolyzer indicate good visual repeatability in terms of peak presence/absence, number of peaks, and retention time between the D3 oligomer (RT between 4.00 and 5.00 min) up to 15 min (Fig. 3A and Fig. 3B). After that, major peaks coming from heavier oligomers, more specifically D8 and D9, shifted between the various replicates (Fig. 3C). These peaks were still integrated for the semi-quantitative analysis.

A tenfold difference in abundance between the filament (20,000) and the furnace pyrolyzers (200,000) was observed, which may be attributed to the use of a transfer line for the filament. Although the transfer line is maintained at 300 °C, it is likely that compounds are recondensed as they leave the pyrolysis furnace and retained in the transfer line. Therefore, they are either not fully injected into the column, or undergo secondary or recombination pyrolysis. Given the results obtained in casework and issues detecting silicone oligomers other than D3 in real samples, the use of a furnace pyrolyzer installed directly over the GC injector is recommended over a filament pyrolyzer coupled to a transfer

line.

From a comparative standpoint, pyrograms obtained with both the filament and furnace pyrolyzers exhibited eight major oligomers (D3-D10) resulting from silicone degradation. The general pattern is quite similar, with these compounds predominantly featured in the pyrograms.

Notable variations were observed in the minor components and pyrolysis products between the two instruments. Particularly, pyrograms obtained with the filament pyrolyzer exhibited a greater number of peaks compared to those acquired with the furnace pyrolyzer.

Distinct variations were observed in peak heights and ratios of major oligomers and minor peaks between the filament and furnace pyrolyzers. Nevertheless, a comprehensive discussion of the actual differences will be undertaken in the semi-quantitative section, employing integrated peak areas for a more precise comparison and thorough investigation of reproducibility.

#### Semi-quantitative comparison

The compositions of all samples were slightly different, as some peaks were not identifiable in all the pyrograms. Compound selection for the semi-quantitative comparison was limited to compounds with a RRT between 0 and 16.00 min (Fig. 1), that were present in all pyrograms,

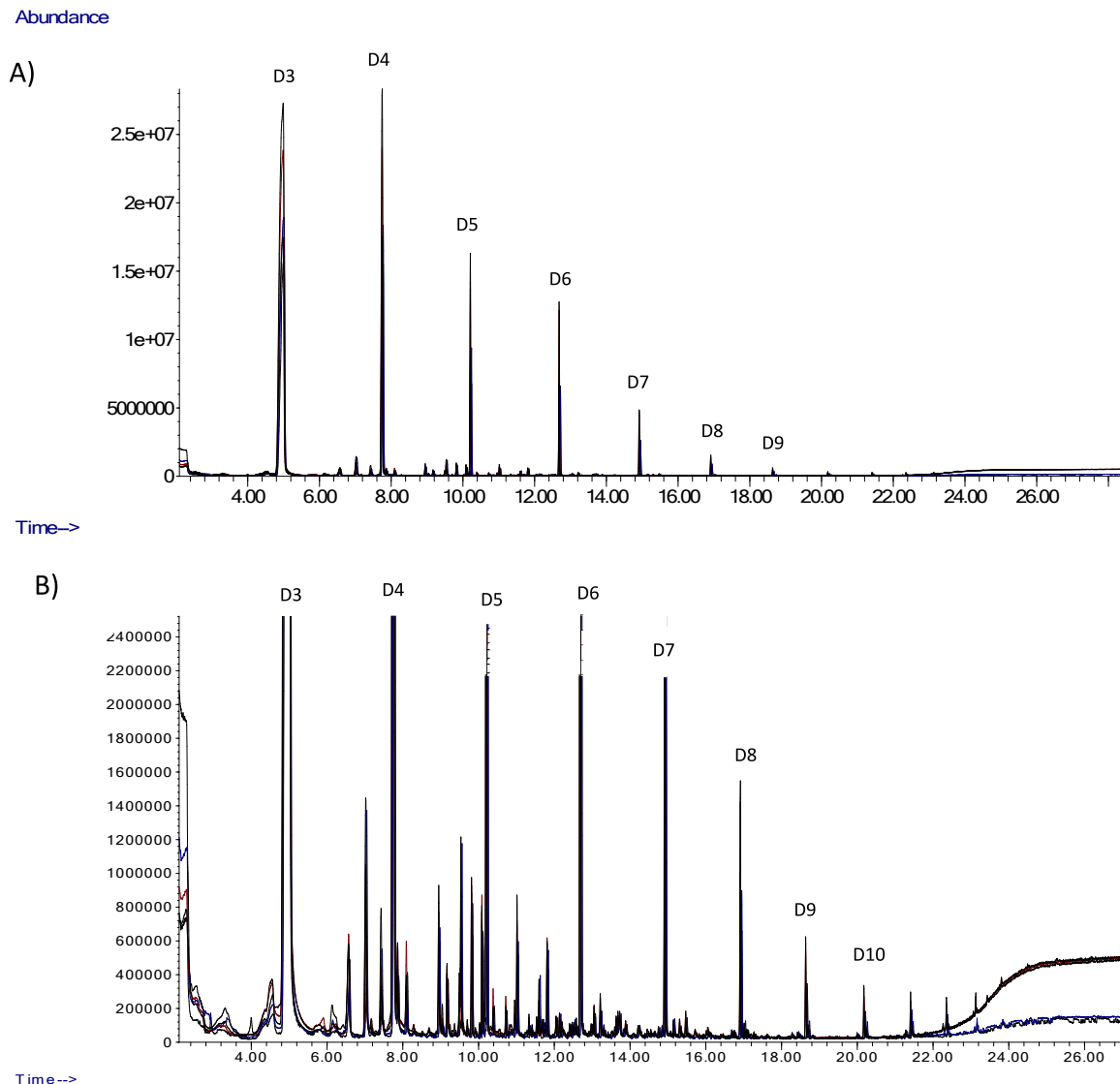
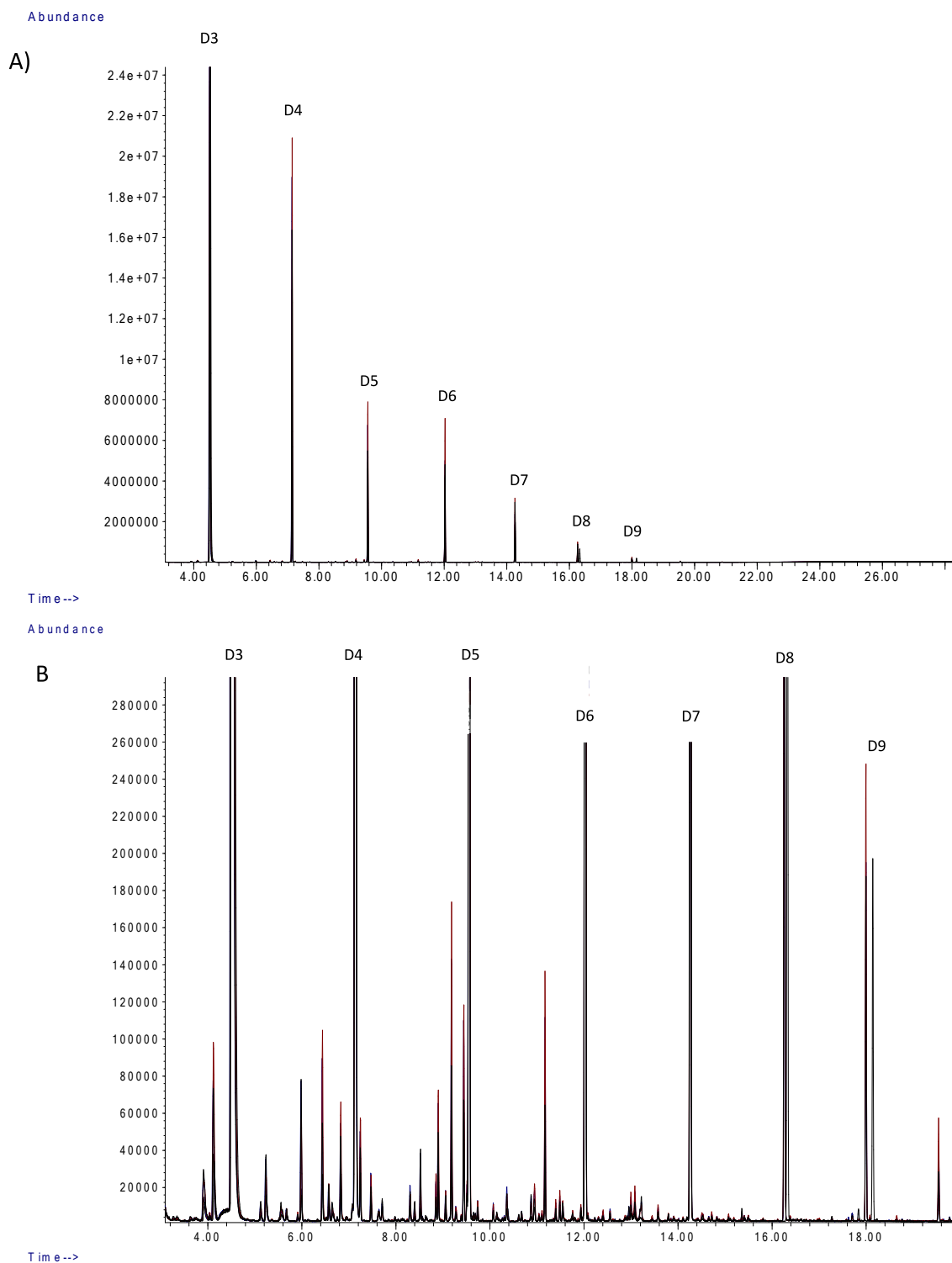


Fig. 2. Illustration of the replicates ( $n = 5$ ) for Manix Strawberry sample, acquired on a furnace pyrolyzer (isothermal oven Frontier Lab. Py-3030S single shot pyrolyzer) device coupled to an Agilent GC 7890B system. A) Full chromatogram. B) Chromatogram focused on the minor compounds.



**Fig. 3.** Illustration of the replicates ( $n = 5$ ) for Manix Strawberry sample, acquired on a resistively heated filament (Pyroprobe 5150 from CDS Analytical Inc.) coupled to an Agilent 6890 N GC system interface. A) Full chromatogram. B) Chromatogram focused on the minor compounds. C) Focus on the shift of D8 and D9 between replicates from a same condom type.

and with a relative abundance sufficient to allow proper distinction from the background (Table 2).

The major oligomers D3-D8 were treated on their own to highlight any major differences in terms of ratios. The choice of using only these oligomers in a first step was based on the experimental design from the literature [21]. Statistical tests highlighted that the means obtained for

each oligomer in all the different samples were found to be statistically different between the two pyrolysis units, with a higher integrated abundance using a furnace pyrolyzer. Reproducibility was investigated using the coefficient of variations obtained for each oligomer in each sample. Table 3 displays the results obtained as a function of the pyrolysis unit used.

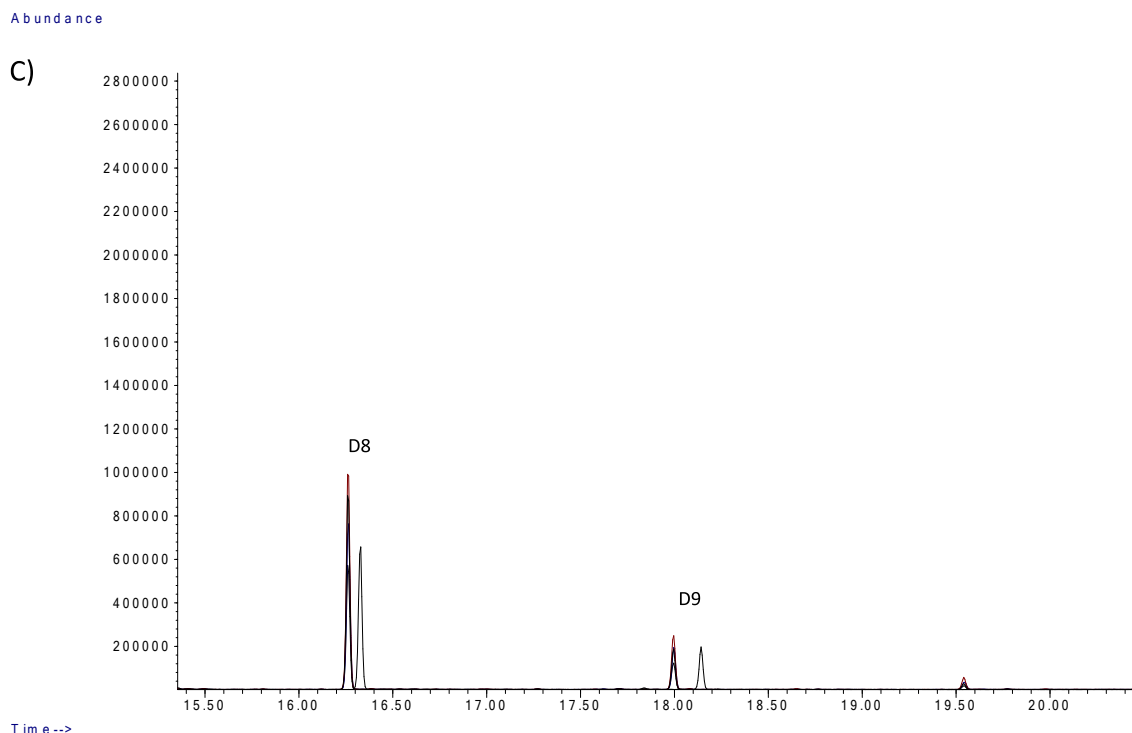


Fig. 3. (continued).

Table 3

Coefficient of variations [%] obtained after processing the data using areasum normalization followed by double square root. Data are displayed as a function of the condoms analysed and the type of pyrolysis unit. Fi: filament pyrolyzer; Fu: furnace pyrolyzer.

Sample pyrolyzer	Durex natural		Ceylor Blue		Manix Skyn		Manix Strawberry		Manix Orgazmax	
	Fi	Fu	Fi	Fu	Fi	Fu	Fi	Fu	Fi	Fu
D3	0.74	0.61	2.29	0.10	1.60	0.18	1.10	0.103	1.77	0.56
D4	1.54	2.54	5.08	0.26	4.37	0.26	2.08	0.26	7.19	2.04
D5	2.62	3.52	6.05	1.12	4.84	1.01	3.35	1.25	14.63	2.07
D6	2.95	1.08	9.51	2.87	6.52	0.93	4.06	2.87	29.34	2.20
D7	3.97	3.05	18.66	1.98	13.82	2.83	4.64	1.99	34.37	4.04
D8	3.99	0.48	22.80	0.72	18.61	2.21	3.53	0.72	44.16	4.28

Data obtained with a filament pyrolyzer were found to present a good reproducibility in the lower oligomers D3-D5, with CV% mostly lower than 10%, except for one condom (Manix Orgazmax) for which D5 presented a 14% CV. With increasing oligomer size, the variability increases, and so does the CV%, raising up to 44% variation for a D8 oligomer. No association could be made between the type of condom (and therefore their composition) [22,30,31] and variability: Durex natural, Ceylor blue and Manix Skyn are classic condoms lubricated with undistinguishable lubricants; on the other hand Manix Strawberry and Manix Orgazmax are special condoms, with flavorings or lidocaine/benzocaine added to the lubricant [30,31]. If the presence of anesthetics could explain the higher variability of Manix Orgazmax, the higher variability of Ceylor Blue and Manix Skyn compared to their classic homologue Durex Natural is hardly explainable by composition differences.

The furnace pyrolysis unit provided results with a reproducibility lower than 5%, independently of the oligomers or the type of condoms, with the highest CV% being around 4.5%. Variations between condoms analyzed were close to none, except for the Manix Orgazmax condom that presented a slightly increased CV% for the bigger oligomers.

Our data indicate that the furnace pyrolyzer exhibits greater reproducibility compared to the filament pyrolyzer, with a tenfold lower CV% that tends to decrease with increased oligomer size. Multiple causes may explain such differences, which are mostly factors of the analytical

setup. Primarily, the filament pyrolyzer presents a significant challenge in terms of sample deposition into the quartz tube. Achieving precise placement on the glass wool without touching the tube walls proved to be quite challenging, compromising repeatability. Additionally, the amount of quartz wool, manually folded around the middle of the tube is likely to be variable, thereby affecting the adsorption and/or desorption of the residues added. In contrast, a furnace pyrolyzer equipped with stainless steel cups facilitates a more homogeneous deposition process, offering greater robustness and consistency.

Finally, the presence of a transfer line joining the filament pyrolyzer to the gas chromatograph increases the residence time of the pyrolysis products, with heavier compounds taking more time to reach the GC injector, therefore promoting secondary by-product formation and increasing the variability of the higher oligomers. The use of a low flow at 1 mL/min coupled to splitless injection mode has a significant impact on the recombination products and residence time in the furnace [29]. Taking into consideration all these observations, when focusing solely on major oligomers, furnace pyrolyzers prove to be more suitable than filament pyrolyzers for the analysis of condom traces.

Coefficients of variation obtained from the 17 compounds integrated in all the replicates of each sample were then considered. A strong variability was again observed in samples acquired with filament pyrolyzer, with CVs far above the 10% acceptable limit for 11 out of 17 compounds extracted. From the samples acquired with a furnace



pyrolyzer, only one observation coming out of one compound reached the 10% acceptability limit, the rest of them being between the 0.5 and 5% range. These observations suggest that, even with a low flow rate within the pyrolysis unit, the recombination process, if it occurs, is more reproducible than within a transfer line and may pose difficulties in its removal from the pyrolysis principle itself.

Finally, when undertaking analysis of forensic evidence, the limit of detection should be established, due to dilution and matrix effects within the vagina. As published by Burnier et al. (2021), limits of detection of 0.01 mg/mL were obtained with a furnace instrument [22]. No limits of detection were reported for the filament pyrolyzer, given the challenges of depositing a liquid in an open tube. In a commonly undertaken second step, if the experts need to distinguish different brand and/or models, the discrimination of the samples should be investigated [21,22].

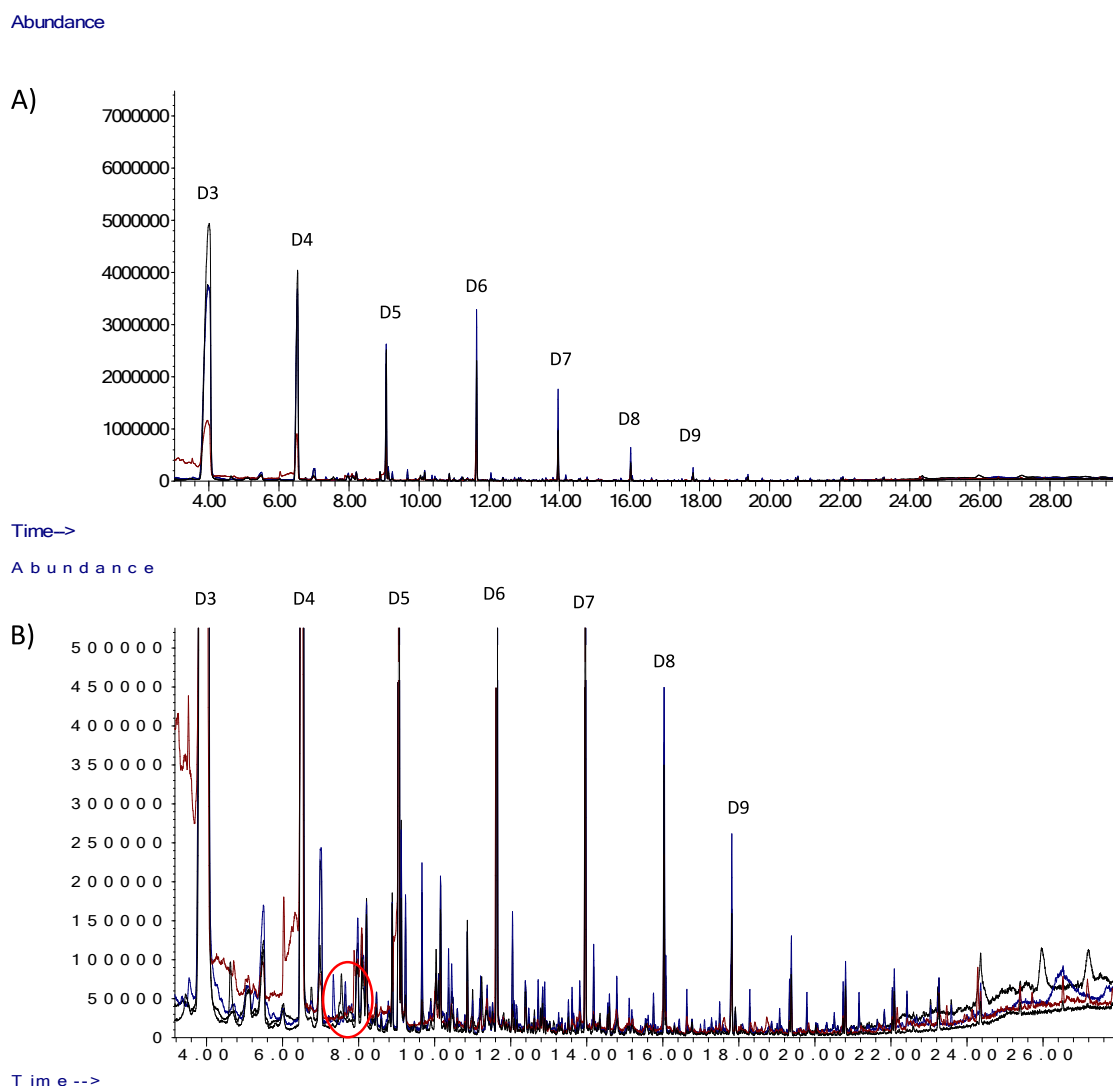
#### Preliminary observation on the impact of the column

Column selection is usually linked to the type of solvents used for extraction. Previous studies have reported multiple combinations of solvents and columns: the use of an apolar column with an apolar

extraction solvent (hexane) [21,22], a mid-polar solvent with apolar column [5], apolar solvent on a mid-polar column and mid-polar solvent on mid-polar column [13]. In this study, the focus was on an apolar solvent (i.e. hexane) as the preferred extraction solvent type for condom residues in casework samples [6,13]. This section is based on only two samples, serving as a preliminary observation. All the experiments described here after were carried out on the furnace pyrolyzer.

#### Qualitative evaluation

Overlay of the results obtained for both samples using a DB-1701 (mid-polar) column showed good repeatability of the major oligomers between the D3 oligomer (RT between 4.00 and 5.00 min) and 22.00 min (Fig. 4A), as well as for the minor compounds (Fig. 4B). After 22 min, column bleed is observed and peaks are not well defined, not repeatable, and often cannot be distinguished from the background. On one of the samples, one minor compound was found to be present only in one replicate (Fig. 4B). As all the other replicates were found to present a good repeatability in terms of minor peaks, it is likely that this peak originates from by-products and recombination due to the pyrolysis itself rather than the column. During the sample characterization, all peaks listed in Table 2 were observed, with slightly varying retention



**Fig. 4.** Illustration of the replicates ( $n = 4$ ) for Migros M–Budget sample, acquired on DB-1701 column used with an isothermal oven Frontier Lab. py-3030S single shot pyrolyzer device coupled to an Agilent GC 7890B system. One replicate encountered technical issue, hence only four replicates are presented. A) Full chromatogram. B) Chromatogram focused on the minor compounds. The red circle highlights the compound appearing in only one replicate. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

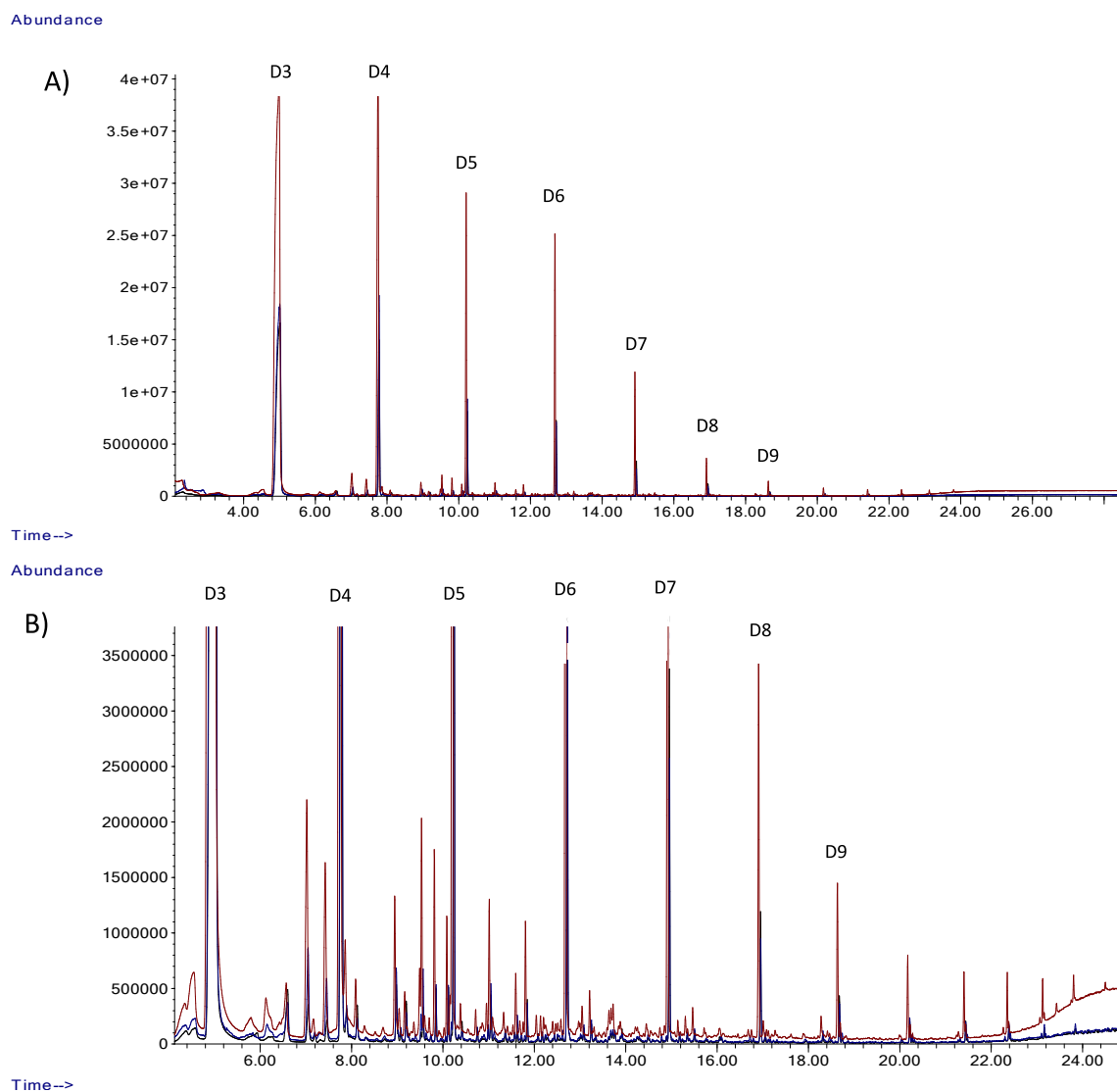
times. At times, this resulted in increased coelution, making the peaks more challenging to integrate for subsequent applications.

Data obtained with the apolar column HP-5MS, similar to the data obtained with the mid-polar DB-1701 column, exhibited relatively good repeatability (Fig. 5A and 5B). However, certain peaks around 5.5 min were only detected in one of the replicates (Fig. 5B). After 17 min, it seems that one replicate presents more peaks than the other. However, upon closer inspection of the region in alignment with the other replicates, it became evident that these peaks were consistently present in all replicates, albeit at seemingly varied relative abundances. The baseline was also found to be slightly higher for this replicate than for the others.

Comparing the qualitative results obtained with the different columns, both columns enable the detection of major D3-D9 oligomers, which are critical for condom residues analysis. D3 oligomer is systematically the most abundant oligomer from visual point of view. This is an important characteristic for forensic purposes since D3 serves as the indicator for detecting the presence of PDMS residues in a sample [6]. In addition, previous studies [7,17,23] indicated the presence of this oligomer even with a lower pyrolysis temperature. Therefore, as long as pyrolysis happens at a temperature high enough to degrade PDMS, D3 oligomers might be generated and detected independently of the column

used. A decrease of abundance with increasing oligomer mass was also observed. Notably, the observed pattern shows an almost linear decrease when employing the HP-5MS column, with D5 being more abundant than D6. In contrast, when using the DB-1701 column, D5 was less abundant than D6. The relative abundance on the scale is slightly higher on a HP-5MS column ( $\times 10^7$ ) versus the DB-1701 ( $\times 10^6$ ). This is only from a visual perspective and these variations will be further discussed in the semi-quantitative comparison section. With both columns, two coeluting peaks were observed along with D5 to D13 peaks, the first being a cyclic oligomeric peak. The mass spectra of each coeluted peak were found to be identical, the only difference being the retention time. No database was able to characterize those coelutions that also occurred when running a standard reference of PDMS (PDMS 200cSt, purchased from Sigma-Aldrich). Given the pattern, it is likely that the two peaks are due to cyclic and linear oligomers of smaller PDMS molecules.

A significant number of minor compounds were detected with both columns, although their relative abundances were different. Even if most components appear to be fairly similarly extracted from the condom itself, recombination pyrolysates were found to vary. The two columns separated the residues differently, resulting in different numbers of peaks detected. Results obtained with the DB-1701 column



**Fig. 5.** Illustration of the replicates ( $n = 3$ ) for Migros M–Budget sample, acquired on HP-5MS column used with an isothermal oven Frontier Lab. py-3030S single shot pyrolyzer device coupled to an Agilent GC 7890B system. Two replicates encountered technical issue, hence only 3 replicates are presented. A) Full chromatogram. B) Chromatogram focused on minor compounds.



presented more peaks, but also more coelutions between compounds abundant enough to be used for discrimination purposes. If the HP-5MS column allowed the detection of around 60 to 70 compounds, the use of DB-1701 column allowed the detection of more than 100 compounds, most of them being dimers and trimers likely to originate from the pyrolysis. The separation of dimers and trimers was found to be affected by the column used.

Lower resolution was observed on the DB-1701 column, with more coelution of minor peaks. Changes in the flow rate or the chromatographic parameters may enhance the quality of the resolution, although it may increase the analysis time. Changes in the extraction solvent might also enhance the quality of the resolution. However, the aim of this work was to emulate an existing procedure for casework samples and therefore neither extraction solvent (i.e. hexane) nor the chromatographic parameters were modified.

During the data extraction phase, the samples acquired with the DB-1701 column showed several minor peaks with the same mass spectrum but different retention times. This situation introduced confusion regarding the determination of peak presence or absence. Notably, this phenomenon was not observed on the HP-5MS column. The difference in column polarity may account for this discrepancy, as the DB-1701 is a mid-polar column, impacting selectivity. Both the polarity and selectivity of the stationary phase play a role in peak separation, with dipolar interactions enhancing the separation capacity for compounds with distinct dipolar moments.

#### Semi-quantitative comparison

As with the instrumental comparison, the compositions of each sample were found to slightly differ, and most of the peaks detected could not be identified using the databases. Therefore, comparisons were performed using the main oligomers D3 to D9 to illustrate the semi-quantitative variation due to the different columns used. Reproducibility was investigated using the coefficient of variations obtained for each oligomer in both samples. Table 4 displays the results obtained as a function of the column used.

Data obtained with both columns were found to present a good reproducibility with a CV% lower than 5%, independently from the oligomers. D3-D5 oligomers showed the lowest CV% around max. 0.6 for the DB column, and up to 3% for the HP column. With the oligomers getting bigger, the variability increases, and so does the CV%, raising up to 4% variation for a D8 oligomer.

Comparing data, CV% obtained on the DB-1701 column were found to be almost systematically lower than the ones obtained with the HP-5MS column, suggesting a better repeatability for the DB-1701 column. However, testing hypothesis  $H_0$  (the means are equal) versus  $H_1$  (the means are different) supported  $H_0$  for all the oligomers. Therefore, the choice of the column is not dependent on a statistical difference in the variations of the oligomers, but rather by a question of resolution and solvent type. A rapid test, which should be more thoroughly investigated to confirm our observations, was carried out by modifying the instrument parameters to evaluate if the separation along the DB-1701 column could be enhanced. Results were not conclusive: the analysis time required almost one hour to get adequate separation, which was not satisfactory. For the experimental conditions used in this paper, HP5-MS column is the most suitable as it provides superior peak separation.

#### Conclusion

Condom traces are increasingly recovered from sexual assault victims, and a plethora of analytical protocols for detection and interpretation of these traces have arisen over the past 10 years. Protocols using py-GC/MS typically employ either filament or furnace pyrolysis units. This paper initially aimed to compare both units to determine which was more suitable for analyzing condom evidence. Subsequently, the column type was briefly investigated.

**Table 4**

Coefficient of variations [%] obtained after processing the data using areasum normalization followed by double square root. Data are displayed as a function of the condoms analysed and the type of column. DB for DB-1701 column, HP for HP-5MS column.

Sample	Migros M–Budget		Ceylor Strawberry	
	DB	HP	DB	HP
D3	0.24	0.94	0.03	0.53
D4	0.35	1.12	0.04	1.70
D5	0.63	3.11	0.10	1.81
D6	2.32	1.52	0.38	3.81
D7	2.48	1.40	0.32	4.52
D8	3.40	4.26	0.33	4.44
D9	3.36	3.87	0.52	3.20

Results obtained from the comparison of the two different pyrolysis units highlighted the presence of the major oligomers (D3-D10) and diagnostic peaks originating from silicone degradation, independent of the pyrolyzer type. Significant differences were observed in the relative abundance and presence/absence of minor peaks. The furnace pyrolyzer produced more abundant peaks, while the filament pyrolyzer enabled the detection of a greater number of peaks. Both pyrolyzers exhibited good qualitative repeatability. From a semi-quantitative perspective, significant differences were found in the reproducibility between the pyrolysis devices. The furnace pyrolyzer was more reproducible with lower coefficient of variation, systematically below 5%, compared to the up to 40% variation generated by the filament pyrolyzer.

Results concerning the column type (mid-polar vs. polar) are preliminary due to the limited sample set. However, these results highlighted qualitative differences in terms of peaks and co-elution of the peaks, as the mid-polar column revealed more coeluted peaks and a lower resolution than the polar column. From a semi-quantitative point of view, no statistical differences in the reproducibility of the major oligomers were observed. Therefore, column selection remains up to the analyst, although the recommendations drawn from this preliminary study would be to use a polar column when using a polar extraction solvent. Further research on the use of dichloromethane as an extraction solvent is warranted, despite its known limitation of incomplete extraction [13]. This is particularly important if the laboratory prefers using a mid-polar column.

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#### CRedit authorship contribution statement

**Céline Burnier:** Writing – original draft, Visualization, Supervision, Methodology, Investigation, Data curation, Conceptualization. **Jonathan Maurer:** Writing – review & editing, Visualization, Investigation, Data curation.

#### 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.

#### Data availability

The datasets used and/or analysed during the current study are available from the corresponding author on reasonable request.

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