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Negative results: Investigations into the quantification of silicone-based condom lubricants in solution by DRIFTS-FTIR

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ABSTRACT

Condom (specifically silicone) lubricants are a form of trace evidence being increasingly submitted for examination in forensic investigations of sexual assault. Interpreting these traces requires an understanding of their transfer and persistence, such as being able to quantify the amount of transferred material as well as the loss percentage over time. However, to the best of our knowledge, an accurate quantification method for silicone polymers within a forensic context has not been reported. This study evaluated diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), a commonly used method for qualitative analysis of condom evidence in casework, as an approach for the quantification or semi-quantification of silicone lubricants in solution. Although a general trend was observed between the DRIFTS signal and the silicone lubricant concentration, high variability between sample runs meant that these changes were not reproducible enough for quantitative prediction.

1. Introduction

In forensic casework, analysis of condom evidence is usually focused on detecting silicone lubricants such as polydimethylsiloxane (PDMS), as they are most commonly known to transfer into the vaginal matrix [1–4]. These analyses are routinely carried out using Fourier transform infrared spectroscopy (FTIR) [5–9] and pyrolysis gas chromatography-mass spectrometry (py-GC/MS) [3,4,10] although other methods such as matrix-assisted laser desorption/ionisation-mass spectrometry (MALDI-MS) or direct analysis in real time/time-of-flight (DART-TOF)-MS have also been reported [7,11–15].

In the context of interpreting condom evidence, forensic scientists are frequently questioned regarding the presence or absence of silicone traces. Such interpretation partly relies on the existence of transfer and persistence models on the amount of silicone transferred from a condom into the vaginal matrix and the degradation kinetics with time. These models, as described in literature regarding other types of evidence [16–20], usually rely on the quantification of the target compound or trace material. There is hence a need for quantification studies of silicone traces, validated according to ISO17025 norms, so that transfer and persistence questions relating to condom evidence can be addressed. The creation of transfer and persistence models would allow forensic experts to evaluate their findings with respect to a Bayesian approach [21–24]. However, to the best of our knowledge, none of the previously reported methods for condom lubricant analysis have been used for an accurate quantification nor semi-quantification of silicone extracts.

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) is a powerful screening method that has been reported for multiple investigations into condom evidence [5,8,9,25]. DRIFTS-FTIR is ideal for the analysis of silicone extracts from condom traces as it is rapid, non-destructive, and requires minimal sample preparation. It also enables analysis of both liquid and solid samples that are difficult to analyse in transmission mode, as is often the case with condom residues [8]. Previous studies using DRIFTS-FTIR have shown that the degradation of silicones between 6 and 24 h post-coïtus can be visibly observed in the DRIFTS spectra [8,26]. It is therefore feasible that DRIFTS could be used for the quantification of silicones, enabling development of transfer and persistence models. A valid quantification method using DRIFTS-FTIR would be of significant interest in a forensic interpretation view: as formerly illustrated by Saric et al. (2021) and Fischer et al. (2021) [26,27] who were investigated transfer and persistence of silicone-based lubricants in sexual intercourses, the obtention of accurate quantification for transfer and persistence studies would enable to enhance the quality of the models built and investigate further the mechanisms involved in both transfer and persistence.

However, absolute quantification of condom evidence is challenging due to the presence of a biological matrix that may cause interferences. In these cases, it may instead be possible to develop semi-quantitative approaches to determine relative quantities of material present. This has been achieved in other areas of forensic analysis, such as determining approximate ages of latent fingermarks [28] or analysis of dye concentration in fibres [29]. In both studies, exploratory techniques such as PCA and HCA have been used for their semi-quantitative purposes, this in complement to having full quantification performed at the same time.

This study investigated the applicability of DRIFTS for quantitative and semi-quantitative analysis of PDMS as a target silicone polymer in solution. Five-point calibration models were constructed using partial least squares regression (PLSR) and evaluated using one-way ANOVA and prediction of a separate validation set. PCA was then investigated as a semi-quantitative approach to discriminate relative concentrations of silicone in condom lubricant samples.

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2. Material and methods

2.1. Chemical and reagents

Hexane (Sigma-Aldrich) was used as received. PDMS 200 cSt was purchased from Sigma-Aldrich (CH) and used as a reference standard. Cotton swabs (150 C) were purchased from COPAN (USA). Potassium bromide (analytical grade) was purchased from Fluka Chemika and was manually grinded to obtain a homogenous powder before use.

2.2. Solutions and simulated samples

A standard solution of PDMS (100 mg/mL), with additional dilutions at 10, 3, 2 and 1 mg/mL, were prepared to develop simulated casework samples. A further set of standards with concentrations ranging from 0.1 to 1 mg/mL were prepared as quantification samples.

To prepare simulated casework samples, cotton swabs were spiked with 1 mL of standard PDMS solution at concentrations of 3, 2 and 1 mg/mL. Swabs were left to dry before being cut at the base of the wooden stick, deposited in a glass vial and extracted with 1 mL of pure hexane. The vials were vortexed for 1 min and then sonicated for 15 min.

Homogenised KBr was deposited into metal sample cups and strong pressure applied to remove residual air. The resulting pellet batch were stored in a 100 °C oven until use. 10 µl of each swab extract were spiked onto a pellet which was then placed in a 100 °C oven for 15 min to evaporate the solvent. Blanks were prepared in the same manner using 10 µl of hexane and analysed every 3 scans to account for background interference. Extraction blanks were also prepared in the same manner using extraction of a blank swab.

2.3. Calibration and validation samples

A five-point calibration curve was built using standard solutions of 0.1, 0.25, 0.5, 0.75, and 1.00 mg/mL PDMS, with standards analysed in triplicate. Calibration standards were run prior to any sample analyses, and for the purpose of the study were run once a week. Three calibration series were run on different weeks, leading to a total of 45 calibration-point analyses (5 standards x 3 replicates x 3 time points). An external validation set was also prepared, consisting of standard solutions with concentrations between 0.1 and 1.00 mg/mL PDMS (at 0.1 mg/mL intervals), which were similarly analysed in triplicate on different days.

2.4. Instrumentation and analytical conditions

Infra-red spectra were acquired with a Digilab FTS 3000 Excalibur FTIR spectrometer, equipped with a Spectra-Tech 0030–05 Collector II diffuse reflectance accessory and DTGS-KBr detector. Data collection was carried out using Resolution Pro (v.4.0, Agilent Technologies) software. Spectra were collected in transmission mode over the 4000–400 cm^{-1} spectral range, with 4 cm^{-1} resolution and 64 co-added scans. Spectra were subsequently converted to absorbance units for pre-processing and chemometric analysis.

2.5. Statistics

Spectral pre-processing and chemometric analysis were carried out using The Unscrambler X (v. 10.1, Camo Software, Norway).

A total of 20 different pre-processing treatments were investigated. The two most important ones are presented in the paper and the 18 other are available in Supplementary Information. For each combination, a linear partial least squares regression (PLSR) model was built from the calibration samples using the non-linear iterative partial least squares (NIPALS) algorithm and the 1300–700 cm^{-1} spectral range. The coefficient of determination (R^2) for calibration and prediction within each model was determined via cross-validation, with one-third of samples randomly selected as the prediction set. The pre-processing protocol producing the highest R^2 was then used to predict concentrations for the external validation samples.

Semi-quantification was carried out using principal component analysis (PCA) to see if discrimination could be achieved between different concentration ranges of PDMS in solution. PCA was first performed on the raw spectra from the calibration and simulated casework samples. This process was then repeated using twelve pre-processing methods (see Supplementary information) to see if this provided enhanced separation of samples. All PCA models were carried out on mean-centred spectra using the NIPALS algorithm. Samples were plotted against combinations of up to the first seven principal components (PCs), to determine whether any clusters based on their PDMS concentration range could be visually distinguished.

3. Results and discussion

3.1. Preliminary considerations

A 1 mg/mL PDMS solution was initially analyzed to confirm the diagnostic peaks. PDMS presents four major peaks (Fig. 1) attributed to Si-C stretching (1263 cm^{-1}), Si-O-Si asymmetric stretching (1097 and 1021 cm^{-1}) and dimethyl and trimethyl symmetric deformation (801 cm^{-1}). As all these peaks fall within the 1300–700 cm^{-1} spectral range, PLSR models were built using only this range of the spectrum. An internal standard was not used in preparing the samples, due to the nature of the workflow of analytical instruments. Silicone-based lubricants would be analysed using py/GC-MS, which would cause the internal standard to degrade and interact with the residues generated during the pyrolysis of silicones. Therefore, casework will not be analysed with an internal standard, as this would complicate interpretation of the results obtained for condom lubricants.

The results obtained from chemometric analysis are highly dependent on the data pre-processing. Common pre-processing methods for FTIR data include baseline corrections, first or second derivatives, as well as scatter corrections [30–36]. Scattering corrections include multiplicative scatter correction (MSC), which corrects for additive and/or multiplicative effects (e.g. due to particle size) through normalisation against a reference spectrum; or standard normal variate (SNV), which centres and reduces the data without the need for a reference spectrum. Unit vector normalisation and range normalisation are often recommended [37–42], with the former being more routine. For diffuse reflectance spectra, it is also common to perform a Kubelka-Munk (K-M) transformation, which is recommended as the optimal way of deriving quantitative information [43–45].

In this study, a total of 20 different pre-processing combinations were evaluated to determine the most ideal approach for deriving quantitative information from the DRIFTS spectra (see Supplementary Information). A baseline correction and normalisation followed by K-M transformation gave the best results, so this approach was used for all further statistical analyses.

3.2. Development of quantification method using PLSR

Quantitative PLSR models were constructed using standards of 0.1, 0.25, 0.5, 0.75 and 1.0 mg/mL PDMS. Each standard was analysed in triplicate at three different time-points, resulting in a total of 45 calibration analyses. The spectra underwent a baseline correction to account for dispersion effects and unit vector normalised to reduce random variability from the surface texture of the KBr pellets. All spectra were then adjusted to a maximum reflectance of 1 because the K-M function does not handle values close to 0, like those obtained using normalisation [46]. The K-M conversion was then applied according to the equation:

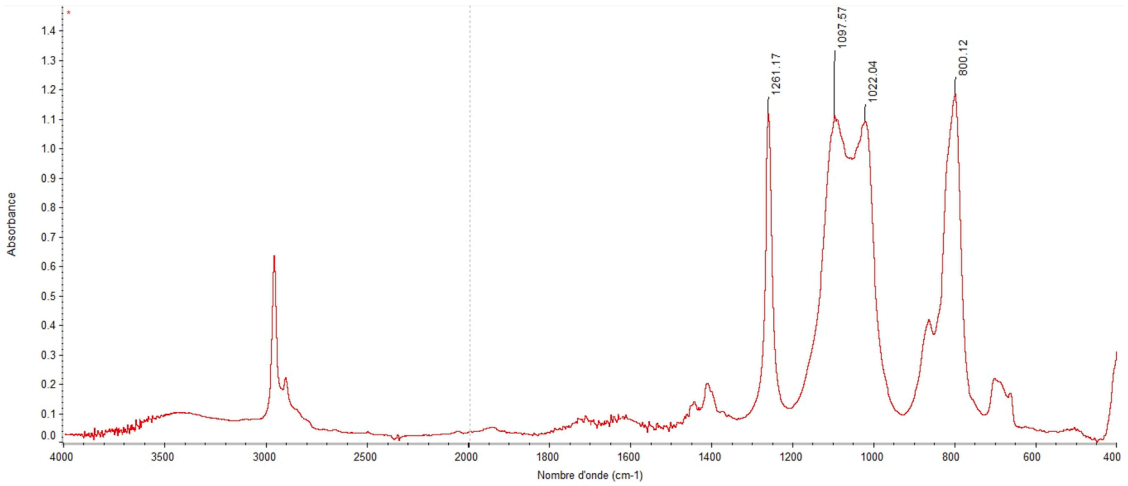

Fig. 1. DRIFTS-FTIR spectrum of PDMS 200 cSt standard, diluted at a concentration of 1 mg/mL.

$$F(R) = \frac{(1-R)^2}{2R} \quad (1)$$

The overall model constructed using the K-M converted data using all 45 calibration analyses is presented in Fig. 2.

Results obtained for the regression and prediction for each of the tested calibration curves (those obtained at three different time-points and the overall model combining all calibration analyses) are shown in Table 1.

The coefficient of determination (R^2) exceeded 0.96 for each individual calibration series, but decreased slightly to 0.94 when pooling the data from the combined series. Since each set of calibration measurements were acquired one week apart, this suggests that variations between sample runs might affect the calibration quality. A strong difference in the R^2 between regression and prediction is also observed, with all the prediction coefficients being smaller than the regression ones. When observing the root mean square error (RMSE) obtained for both regression and prediction, the errors are similarly smaller on the regression than on the prediction metrics. This suggests that although there are changes linked to the concentration of the sample itself, these changes are not reproducible enough for accurate predictive purposes.

An approximate detection limit was estimated by analyzing progressive dilutions of a PDMS solution down to a concentration of 0.001 mg/mL. The four main diagnostic peaks for PDMS had to be visible, with a signal-to-noise (SNR) over 3, for PDMS to be deemed present. Using these criteria, the smallest concentration still detectable was 0.005 mg/mL. This result was confirmed by analyzing eight replicates at 0.005 mg/mL, which all yielded consistent profiles. Although the diagnostic peaks were visible in the 0.001 mg/mL solution, they were not within a SNR over 3. The limit of detection was therefore estimated at 0.005 mg/mL which is significantly lower than the results obtained by Burnier et al. (2020) with the same instrumentation [47].

Table 1
Regression and prediction coefficient for each calibration curve.

	Regression		Prediction	
	R^2	RMSE	R^2	RMSE
Serie_01	0.988	0.035	0.863	0.129
Serie_02	0.965	0.0604	0.940	0.0855
Serie_03	0.994	0.0235	0.956	0.0732
All_data	0.941	0.078	0.871	0.125

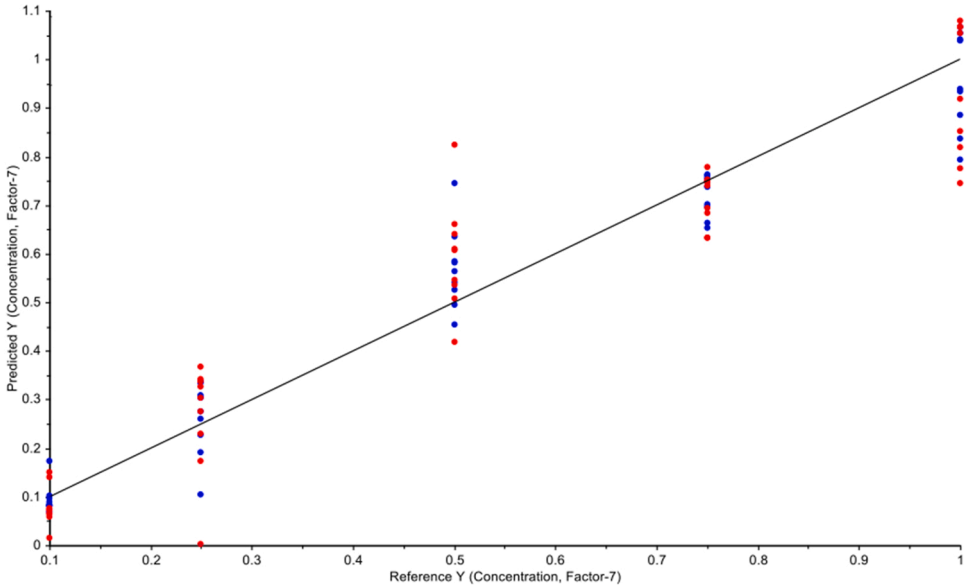

Fig. 2. Linear regression after Kubelka-Munk processing, 45 spectral acquisition, wavelength domain 1300–700 cm^{-1}. Black line is the trend line for X=Y.

3.3. Validation of the quantification procedure

Evaluating the performance of a quantification model using cross-validation can be misleading, as the same data is used to both build and test the model. Because of this, a separate set of validation samples with concentrations between 0.1 and 1.0 mg/mL (at 0.1 mg/mL intervals) were also predicted using the developed PLSR models. These samples were analyzed in triplicate on the same and different days to the calibration samples.

Validation parameters were determined using one-way analysis of variance (ANOVA), with the results shown in Table 2 [48,49]. The 0.1 and 0.2 mg/mL results were excluded because the coefficients of variation (CV) were very high, at 97% and 148% respectively. The precision for each sample was determined as the global standard deviation (SD), taking into account both the intra-group analysis variance (standard deviation within samples, SDWS) and inter-group analysis variance (standard deviation between samples, SDBS). In addition, the ratio between the mean measured concentration (MMSC) and the analyzed standard concentration (ASC) was calculated to obtain the mean recovery (MR) percentage.

CVs ranged between approximately 0.05% and 60%, indicating that measurement precision was highly variable. The average recovery rate was 70.85 (±22.16) %, which does not cover an acceptable area of analysis. Indeed, average recovery rates are generally of the order of 100 ± 20% [36,38]. Only one area of the curve between 0.3 and 0.5 mg/mL corresponds to these criteria.

To better demonstrate these issues, an accuracy profile has been drawn (Figure A) to relate the calculated concentrations (MMSC) to the true concentrations (ASC). There is a substantial difference between the calculated and true concentrations, particularly for samples at the extreme ends of the concentration range, which is generally indicative of a bias in the method. In Fig. 3A, the acceptance limit values (within ± 20% of the true value) are also drawn. Concentrations from 0.4 to 0.6 mg/mL have predicted values close to their true value, and errors that fall within these acceptance limits, while the remaining standards do not fit within the acceptance domain. This can be attributed to a high level of variation between ample runs, shown in Fig. 3B and C for the 0.3 mg/mL and 0.9 mg/mL standards.

For validation samples analyzed in a different run to the calibration samples, the error rate was over 10%, with concentrations systematically over- or underestimated. For example, samples containing 1 mg/mL of PDMS were quantified at 0.75 mg/mL, or samples from 0.9 mg/mL were quantified at around 0.3 mg/mL. However, when validation samples were analyzed on the same day and within the same preparation batch as the calibration standards, the error rate dropped below 10%. Notable variations were also observed between repeats of the same solution analyzed by a single operator at different times. This is consistent with previous findings by Sirita et al. [50] who reported a spread of intensity values when performing measurements of a sample at different time points. This was linked to the difficulty of obtaining reproducible sample packing in DRIFTS analysis, and the fact that the proportion of adsorption sites in the sample affects the concentration and thus the signal.

Based on previous observations made by Sirita et al. [50], several hypotheses may help explain the lack of repeatability of the analytical instrumentation. Given that reproducible analysis of PDMS standards has been achieved using other infrared techniques such as ATR-FTIR [47,51], this variation is most likely linked to sample preparation. First, the grinding and compaction of KBr is operator-dependent, varying between pellets as well as between preparation batches. There is also potential evaporation of the solvent in the syringe before deposition onto the pellet, given the high volatility of hexane. At the time of the deposition of the sample on the KBr, a deformation of the surface of the pellet was observed, which could cause variations in light reflection and scattering that would not occur reproducibly. Previous studies reporting the successful use of DRIFTS for quantification used solids mixed directly with KBr prior to analysis [34,44,46,50,52], so the pellet surface would likely have remained flat and not modified prior to analysis. Finally, the results of the DRIFTS analysis are also influenced by the position of the pellet in the sample holder, which may slightly vary between the analyses, resulting in a modification of the angle of incidence of the laser.

It was concluded from these experiments that although there was a distinct correlation between the concentration of silicone polymers in solution and their DRIFTS spectra, reliable quantification in accordance with analytical reference standards [34–36,53–58] was not achievable due to lack of measurement repeatability. On that basis, it was decided to instead consider a semi-quantitative approach that might allow estimation of the relative quantity of silicone lubricant (i.e. PDMS) present within a condom trace sample. Such an approach has already been developed with py-GC/MS for condom evidence as well as other types of evidence such as tyre traces as illustrated in [59–62] and such approaches were found to be successful in casework studies [63] as well as in casework simulation studies [26,27].

3.4. Semi-quantitative investigation

Previous studies have shown that where precise quantification is not possible, it may be possible to instead give an idea of the range of concentration (i.e. semi-quantification) using exploratory techniques such as PCA.

PCA was first carried out on the raw data from both the calibration samples (with known concentrations between 0.1 mg/mL and 1.00 mg/mL) and the simulated casework samples (spiked with standard solutions at concentrations of 3, 2 and 1 mg/mL). The raw spectra were used as pre-processing could inadvertently remove intensity variations due to differences in PDMS concentration. It was assumed that if there were differences in the raw absorbance intensities due to different PDMS concentrations, the resulting scores plots would discriminate samples belonging to different concentration ranges. However, as seen in Fig. 4, no specific clusters were observed based on the raw data.

12 different pre-processing schemes were subsequently tested to determine whether they produced any visible clusters, with scores plots produced for each (see Supplementary Material). A slight improvement was noted when using first and second derivatives in that some samples formed distinguishable clusters, but these clusters could not be associated with the concentration of the samples. Ultimately, none of the pre-processing combinations were successful in discriminating samples according to their concentration. These results highlight that DRIFTS, although a very sensitive method for the detection of silicone polymers in condom lubricants, should be used in conjunction with other techniques such as py-GC/MS for quantitative purposes. Absolute

Table 2
Validation parameters using One-way ANOVA.

ASC (mg/mL)	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
MMSC (mg/mL)	0.16	0.38	0.47	0.54	0.28	0.45	0.46	0.81
MR (%)	54.71	96.21	95.01	90.00	40.85	56.62	51.72	81.65
SDWS (mg/mL)	0.064	0.094	0.138	0.188	0.143	0.203	0.172	0.150
SDBS (mg/mL)	0.088	0.111	0.147	0.176	0.154	0.178	0.191	0.142
SD (mg/mL)	0.018	0.00023	0.00062	0.00035	0.171	0.120	0.188	0.033
CV (%)	11.24	0.05	0.13	0.66	59.95	26.57	40.55	4.12

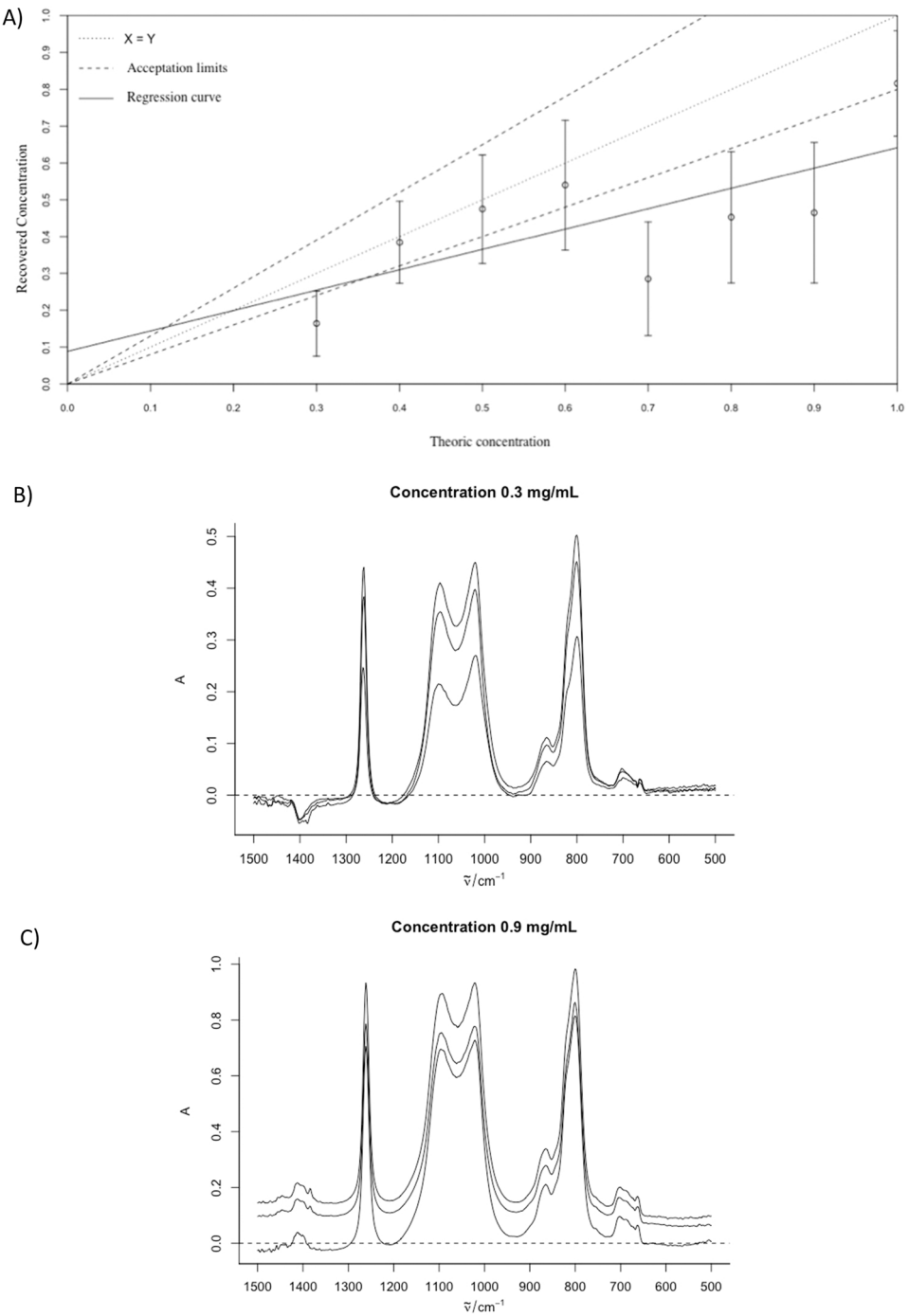

Fig. 3. A) Accuracy profile, plotting the theoretical concentration as a function of the recovered concentration; B) Example spectra of 0.3 mg/mL samples; C) Example spectra of 0.9 mg/mL samples.

quantification of real samples would also be challenging, because the sampling varies according to the person that collects the traces. The swab performed will not necessarily be representative of the contents of the vaginal matrix or the exact concentration and depends on several uncontrolled parameters.

4. Conclusion

The forensic interpretation of condom residue evidence requires the development of quantitative approaches that can help understand transfer and persistence mechanisms. To date, the quantification of silicone polymer recovered from condom residues, is still pending and has not been reported in the current literature. The present study aimed to investigate the potential of quantification using DRIFTS-FTIR to help the investigation of transfer and persistence of condom evidence.

The development of a quantitative model using PLSR was not successful due to a high variability between runs. Strong correlations in the regression models were observed, showing that there is a systematic trend between the DRIFTS spectra and the PDMS concentration, but this trend is not reproducible enough to use for reliable quantitative predictions. Similarly, general discrimination of samples according to their relative concentrations using PCA was not achieved. Several factors that could affect the obtained results were considered, and it was concluded that sample preparation had a great impact on the possibility of

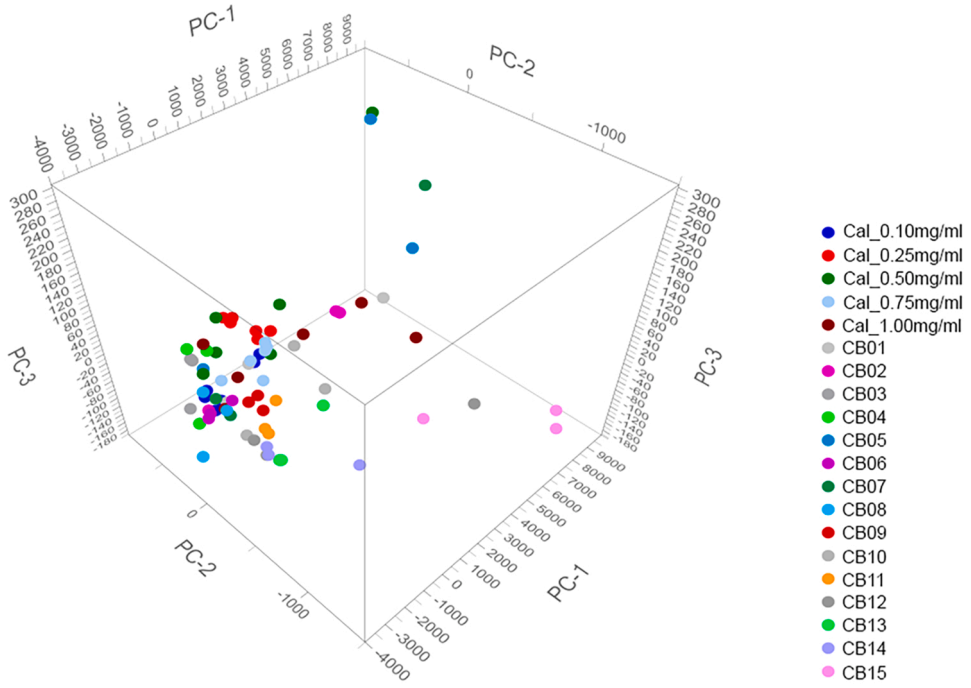

Fig. 4. 3D PCA scores plot showing the distribution of PDMS samples of different concentrations based on their DRIFTS spectra. Raw data, without any preprocessing are presented.

quantification. These observations are constituent with previous findings concerning DRIFTS analysis, due to sample surface texture and modification.

DRIFTS remains a powerful and highly sensitive screening method for qualitative detection of PDMS in condom trace evidence, with a limit of detection around 0.005 mg/mL. However, other methods such as py-GC/MS are currently required to conduct quantitative, or semi-quantitative, analysis.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Georgina Sauzier is a Section Editor of Forensic Science International: Reports. The authors declare no other competing interest.

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.fsir.2022.100283.

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