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Infrared analysis of hair dyeing and bleaching history†

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Forensic examination of hair is commonly performed to trace its origin and make a connection between a suspect and a crime scene. Such examination is based on subjective microscopic analysis of hair. During the last decade, several spectroscopic approaches have been proposed to make forensic analysis of hair more robust and reliable. Surface-enhanced Raman and attenuated total internal reflection infrared spectroscopies allowed for detection and identification of dyes directly on hair and even differentiation between commercial brands of those colorants. However, these is a question that remains unanswered: can artificial dyes be detected on bleached hair or bleaching can be used to fully erase information about hair coloring? In this study, we report experimental results that provide a clear answer to this question. We show that infrared analysis can be used to differentiate between undyed bleached hair and hair that was colored with both permanent and semi-permanent dyes prior to bleaching. We also show that IR analysis can be used to distinguish between undyed unbleached and undyed bleached hair. We demonstrate that in combination with multivariate statistical analysis, IR analysis can be used to distinguish with 96–100% accuracy between those hair classes.

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Introduction

Forensic analysis of hair evidence found at a crime scene is critically important to establish a connection between a suspect and a crime scene or demonstrate the absence of such connection.¹ In most forensic laboratories, hair analyses are carried out by subjective microscopic examination that allows for identification of the biological species from which the hair sample originated, as well as distinguishing hair from organic polymers with similar visual appearance.² Such subjective analyses of hair are often inconclusive. It was recently discovered that in 268 reviewed court cases, in which hair was used as evidence against defendants, 258 contained flawed testimony.³ It should be noted that in 32 out of those 268 cases, defendants were sentenced to death, whereas 14 defendants have been executed or died in prison. These striking facts suggest that more robust and reliable hair analysis procedures should be developed and used in forensic practice.

The first groundbreaking discovery in quantitative hair analysis was reported by Kurouski and Van Duyne.⁴ The researchers used surface-enhanced Raman spectroscopy (SERS) to detect and identify hair colorants. SERS is based on amplification of Raman scattering by coherent oscillations of conductive electrons, also known as localized surface plasmon

resonances (LSPRs).^{5–8} LSPRs can be induced on the surface of noble metal nanostructures upon their illumination with electromagnetic radiation.^{9–11} Kurouski and Van Duyne demonstrated that SERS was capable of distinguishing between undyed and dyed hair, as well as identifying whether hair was colored with semi-permanent or permanent dyes. Following up on their work, Esparza and co-workers showed that SERS could be used to analyze dye on hair even after 9 weeks since the dyeing process.¹² It has been also demonstrated that SERS was capable of detecting underlying colorants on hair.¹² This is critically important if hair was re-colored by another dye prior to the time of analysis.

These findings were independently confirmed by Boll and co-workers using Fourier-transform infrared (FTIR) spectroscopy.¹³ The reported results demonstrated that FTIR could be used as an alternative tool for analysis of dyed hair. Independently, Panayiotou and coworkers showed that FTIR was capable of sensing hair treatment, color and length, as well as distinguishing between eight separate hair donors based on gender and hair treatment.¹⁴ FTIR analysis of hair can also be used for detection of cosmetic residues and unique identification of a suspect.¹⁵ Independently, Manheim and coworkers proposed that ATR-FTIR could be used to differentiate between hair from humans, cats, and dogs.¹⁶

At the same time, there are many questions in spectroscopy-based forensic analysis of hair that remain answered. Specifically, can the information about hair colorants be erased by bleaching? Our experimental findings reported in this manuscript demonstrate that ATR-FTIR is capable of discriminating

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between previously colored and un-colored bleached hair. Moreover, our results indicate that ATR-FTIR can be used to identify whether hair was colored with semi-permanent or permanent colorants before bleaching and even what bleaching agent was used to treat hair. These results show that vibrational spectroscopy can be used to reveal critically important information about hair dyeing history.

Results and discussion

We have found that the IR spectrum of undyed unbleached hair exhibits vibrational bands at 1234, 1410, 1456, 1530, 1645, 2849, 2920, 2936, 2965 and 3290 cm^{-1} , Fig. 1 and Table 1. These bands can be assigned to CH and CH_2 vibrations (1410, 1456, and 2849–2965 cm^{-1}),^{17–19} as well as amide (1234 (amide III), 1530 (amide II) and 1645 (amide I))^{20–22} vibrations of keratin, the major component of human hair, Table 1. The IR band at 3290 cm^{-1} can be assigned to the O–H vibration of water present in hair.^{17,23}

We have found that bleaching results in a major change in the IR spectrum of hair. We observed a decrease in the intensities of nearly all vibrational bands (1234, 1410, 1456, 1530, 1645, 2849–2965, and 3290 cm^{-1}), which can be explained by structural transformations that take place in keratin upon bleaching. In addition to these spectral changes, we have also found an increase in the intensity of the vibrational band at 1041 cm^{-1} , which can be assigned to S–O vibrations of keratin.²⁴ The increase in the intensity of this band points out the increase in the amount of free cysteic acid groups in keratin that were formed as a result of cysteine oxidation by the bleaching agent.²⁴

We have also found that hair colored with a black permanent dye resulted in an increase in the intensities of nearly all vibrational bands (1234, 1410, 1456, 1530, 1645, 2936, 2965 and

Table 1 Vibrational bands observed in the IR spectra of hair and their assignments

Band [cm^{-1}]	Vibrational mode
1041	Vs (S–O) cysteic acid ²⁴
1065	Vs (S–O) cysteine monoxide ²⁴
1234	Amide III ^{20–22}
1410	C–H bending ^{17–19}
1456	CH_2 scissoring ^{17–19}
1530	Amide II ^{20–22}
1645	Amide I ^{20–22}
2849	Symmetric CH_2 stretching ^{17–19}
2920–2963	Asymmetric CH_2 stretching ^{17–19}
3091	C–H stretching ¹⁷
3290	O–H stretching ^{17,23}

3290 cm^{-1}) relative to the intensities of the corresponding bands in the spectrum of undyed hair. Similar spectroscopic changes have been observed in the spectrum of hair colored with a blue semi-permanent dye. However, the change in the intensities of all the above discussed vibrational bands appeared to be much smaller. Also, instead of an increase, a decrease in the intensities of vibrational bands centered at 2936 and 2965 cm^{-1} has been observed. These spectral changes represent a complex change in the hair structure that is caused by its coloring and bleaching. We have also observed an increase in the intensities of the 1041 and 1065 cm^{-1} bands in the spectra collected from both black permanent and blue semi-permanent dyes. This suggests that application of colorants causes oxidation of cysteins of keratin leading to an increase in the amount of free S–O groups.²⁴

IR analysis of previously colored bleached hair showed two distinctly different spectroscopic signatures depending on whether a permanent or semi-permanent colorant was used to

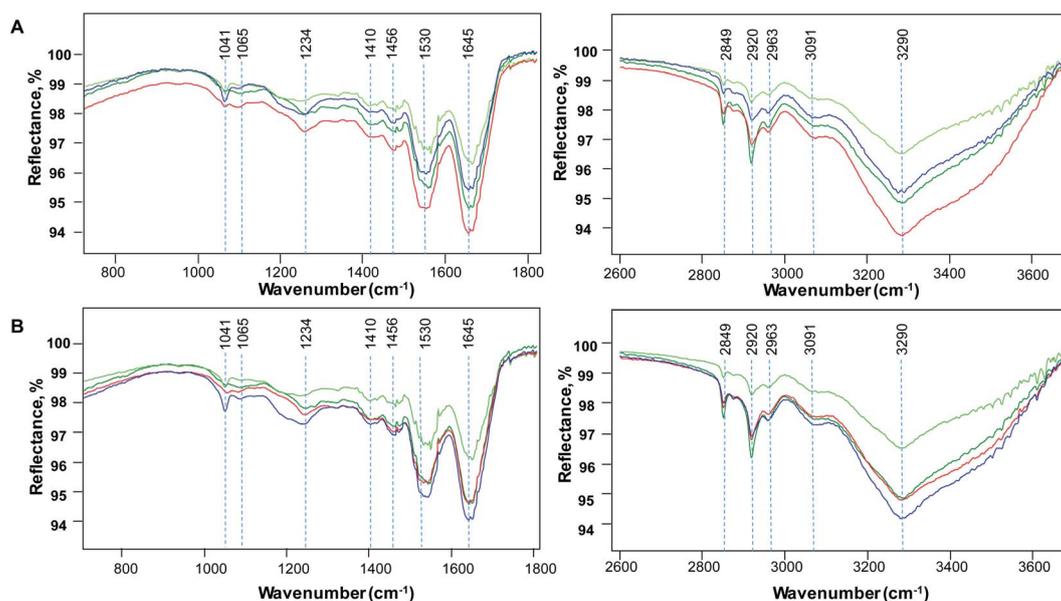


Fig. 1 IR spectra of undyed unbleached hair (green), undyed bleached hair (light green), hair dyed with black permanent (A) and blue semi-permanent (B) colorants (red), as well as hair that was colored and then bleached (blue).

Table 2 PLS-DA confusion matrix of undyed unbleached, and undyed bleached hair, as well as hair that was dyed with a black permanent and blue semi-permanent colorant before bleaching. The PLS-DA matrix also reports the results of hair dyed with black permanent and blue semi-permanent colorants followed by bleaching

	Accuracy	Dyed black permanent	Dyed black permanent-bleached	Undyed-bleached	Dyed blue semi-permanent	Dyed blue semi-permanent-bleached	Undyed-unbleached
Dyed black permanent	100%	20	0	0	0	0	0
Dyed black permanent-bleached	100%	0	10	0	0	0	0
Undyed-bleached	95%	1	0	20	0	0	0
Dyed blue semi-permanent	96%	1	0	0	25	0	0
Dyed blue semi-permanent-bleached	100%	0	0	0	0	19	0
Undyed-unbleached	100%	0	0	0	0	0	20

dye hair initially. In the IR spectrum collected from hair initially colored with a permanent black dye and then bleached, we have found a decrease in the intensities of 1234, 1410, 1456, 1530, 1645, 2849–2936 and 3290 cm^{-1} bands relative to the intensities of the corresponding bands in the spectrum collected from colored hair. The change in the intensities of these vibrational

bands points out the change in the hair color. It should be noted that the intensities of 1234, 1410, 1456, 1530, 1645, 2849–2936 and 3290 cm^{-1} bands in dyed-to-bleached hair were lower compared to the intensities of the corresponding bands in the spectrum of undyed unbleached hair and larger than the intensities of bands in the spectrum of undyed bleached hair.

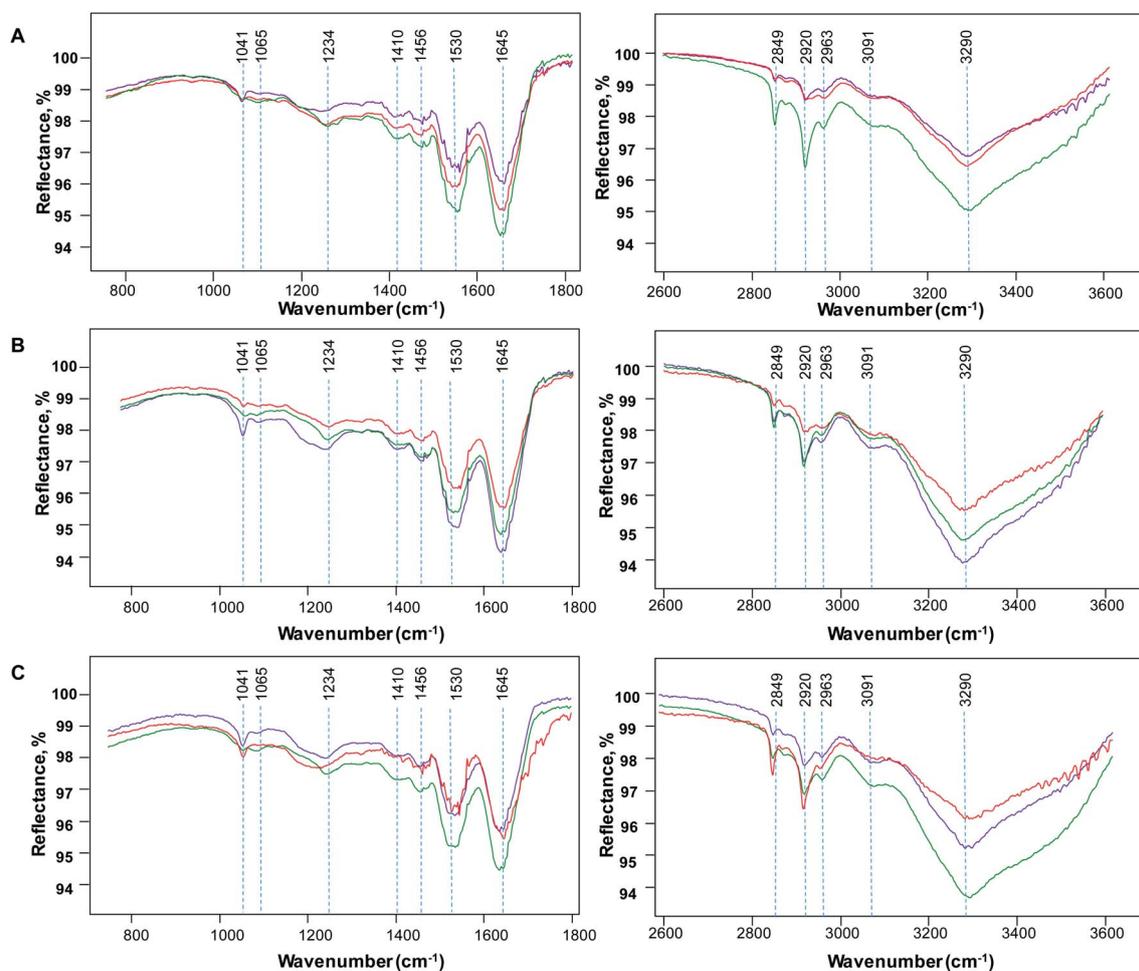


Fig. 2 IR spectra of (A) undyed unbleached hair (green), undyed hair bleached with bleach (purple) and Clorox (red); (B) hair dyed with a blue semi-permanent colorant (green), and hair bleached after dyeing with bleach (purple) and Clorox (red); (C) hair dyed with a black permanent colorant (green), and hair bleached after dyeing with bleach (purple) and Clorox (red).

These spectroscopic changes point out the direct relationship between the intensity of the hair color and intensities of vibrational bands (1234, 1410, 1456, 1530, 1645, 2849–2936 and 3290 cm^{-1}) in its IR spectrum. Also, in the IR spectrum acquired from hair initially colored with a permanent black dye and then bleached, we have observed an increase in the intensity of vibrational bands at 1041 cm^{-1} indicating an increase in the amount of the S–O group that was caused by hair bleaching.²⁴ These spectral changes can be used to differentiate between unbleached and bleached hair colored with a permanent dye.

In the IR spectrum of hair initially colored with a semi-permanent blue dye and then bleached, we have found an increase in the intensities of 1234, 1410, 1456, 1530, 1645, 2920–2965 and 3290 cm^{-1} bands. Similar to the above discussed changes in the spectrum collected from hair initially colored with a permanent black dye and then bleached, we observed an increase in the intensity of 1041 and 1065 cm^{-1} bands associated with bleaching of previously colored hair with semi-permanent dye. These spectroscopic pieces of evidence demonstrate a similar effect of bleach on disulfide bonds in hair colored with both permanent and semi-permanent dyes.

Next, we used PLS-DA to demonstrate that IR analysis can be used for confirmatory diagnostics of hair coloring and bleaching. PLS-DA is a frequently used classification method for spectroscopic data.^{25–32} It combines linear discriminant analysis (LDA) with the multi-collinearity of partial least squares.³³ LDA is a robust method that works by maximizing the ratio of between-class variance to within-class variance to guarantee maximum separation between groups. Our group has demonstrated the power of PLS-DA in plant pest and pathogen detection in numerous systems including corn, wheat and sorghum, and cowpeas, where we could distinguish between infected and healthy tissues with high accuracy.^{25–32} One of the major results of PLS-DA is the loadings plot which allows the experimenter to determine which regions of the spectrum are important for accurate disease detection (Tables 2–6). Our results (Table 2)

revealed 95–100% accurate prediction of spectra depending on their class. Thus, IR spectroscopy coupled to PLS-DA enables highly accurate prediction of whether hair was bleached or not, as well as whether hair was bleached after or before coloring with permanent or semi-permanent dyes.

One may wonder whether the above described spectroscopic evidence is for only professional hair bleach or it can be observed for any commercially available bleaching agents. To answer this question, we investigated the effect of Clorox bleach on undyed hair, as well as hair initially colored with black permanent and blue semi-permanent colorants, Fig. 2. We have found that both bleach and Clorox caused similar structural changes in undyed hair, as well as in hair previously dyed with permanent black and blue semi-permanent colorants (discussed above). PLS-DA confirmed visual differences between the spectra of undyed bleached hair and hair that was colored with both black permanent and blue semi-permanent dyes before bleaching with Clorox, Table 3.

One may wonder whether IR spectroscopy can be used to determine the type of bleach used to treat hair. To answer this question, we used PLS-DA to investigate whether multivariate statistical analysis can be used to differentiate between undyed unbleached hair and undyed hair treated with bleach and Clorox. We also questioned whether IR spectroscopy coupled to PLS-DA can be used to differentiate between hair colored with blue semi-permanent dye and black permanent dye and then treated with bleach and Clorox. Our results (Tables 4–6) show that IR spectroscopy coupled to PLS-DA can be used for 100% accurate differentiation between all those groups of spectra.

These findings demonstrated that IR analysis could be used to detect the presence of artificial colorants on hair, as well as to determine whether hair was bleached or not. We also found that IR analysis of hair could reveal the type of bleach that was used for hair treatment. As was discussed above, the IR fingerprint of hair is dominated by the vibrational bands that can be assigned to proteins (keratin). Therefore, one can envision that such IR-

Table 3 PLS-DA confusion matrix of undyed unbleached hair, as well as hair that was dyed with a black permanent and blue semi-permanent colorant before bleaching by Clorox

	Accuracy	Dyed black permanent-bleached	Dyed blue semi-permanent-bleached	Undyed-bleached
Dyed black permanent-bleached	100%	20	0	0
Dyed blue semi-permanent-bleached	100%	0	20	0
Undyed-bleached	100%	0	0	20

Table 4 PLS-DA confusion matrix of hair dyed with a black permanent colorant before treatment with bleach and Clorox

	Accuracy	Dyed black permanent	Dyed black permanent treated with bleach	Dyed black permanent treated with Clorox
Dyed black permanent	100%	22	0	0
Dyed black permanent treated with bleach	100%	0	10	0
Dyed black permanent treated with Clorox	100%	0	0	19

Table 5 PLS-DA confusion matrix of hair dyed with a blue semi-permanent colorant before treatment with bleach and Clorox

	Accuracy	Dyed blue semi-permanent	Dyed blue semi-permanent treated with bleach	Dyed blue semi-permanent treated with Clorox
Dyed blue semi-permanent	100%	25	0	0
Dyed blue semi-permanent treated with bleach	100%	0	19	0
Dyed blue semi-permanent treated with Clorox	100%	0	0	20

Table 6 PLS-DA confusion matrix of hair dyed with a blue semi-permanent colorant before treatment with bleach and Clorox

	Accuracy	Undyed treated with bleach	Undyed treated with Clorox	Undyed unbleached
Undyed treated with bleach	100%	20	0	0
Undyed treated with Clorox	100%	0	20	0
Undyed unbleached	100%	0	0	20

based detection of colorants and hair bleach is based on structural changes in keratin which are associated with hair dyeing with both permanent and semi-permanent colorants, as well as hair bleaching. It should be noted that IR analysis provides only limited information about the nature of such structural transformation. Alternative techniques such as solid-state NMR spectroscopy, electron microscopy or mass spectroscopy may provide additional details about the nature of chemical transformations of hair keratin that take place upon hair treatment with both dyes and bleach. Nevertheless, we can conclude that such an approach is robust and reliable if used together with PLS-DA. Considering the portable nature of IR spectrometers, such IR-based hair analysis can become a routine in forensic practice.

It is also important to note that IR- and SERS-based diagnostics of hair coloration history have completely different underlying physical principles. The IR approach is based on dye- and bleach-induced changes in the keratin structure (discussed above) and, therefore, can be classified as indirect. SERS, on the other hand, directly detects dyes present on hair. Thus, the SERS approach can be used to build a database of hair colorants, whereas such a database is unlikely to be developed for the IR approach. From the experimental perspective, IR diagnostics can be considered fully non-invasive, whereas SERS requires the application of metal nanostructures on the sample, which makes this analytical approach minimally invasive. Based on these arguments one can envision that both IR and SERS have strong and weak sides in hair analysis. One can envision that the application of both techniques in concert in forensic analysis of hair will likely yield the most reliable conclusions about dyeing and bleaching history of hair.

Conclusions

Our work showed that IR spectroscopy can be used to determine whether hair was bleached or not and if yes, what bleaching

agent was used to treat hair. We also showed that using IR analysis, one can find whether hair was colored before bleaching and distinguish whether permanent or semi-permanent colorants were used. We provided spectroscopic evidence that allows for visualization of all related changes in the hair structure, as well as reported results of PLS-DA that demonstrate high accuracy of IR-based hair analysis. It should be noted that the advantage of this approach is in its non-invasiveness and non-destructiveness, as well as in the possibility of performing it directly at a crime scene by the use of commercially available hand-held IR spectrometers.

Experimental

Hair Samples

Undyed hair samples were collected from three (male, 20–30 year-old) anonymous donors in barbershops of College Station, TX, and used in experiments without any special preparations. The microphotograph of undyed hair is shown in Fig. S1.† The samples were taken from individuals who had no prior history of dyeing their hair. It should be noted that hair of children and senior people may have slightly different structures that will require additional calibration of the FTIR method.

Colorants and Dyeing Procedures

Hair dyes were purchased from a local supply store (Sally's Beauty Supply LLC). Human hair samples were dyed in 50 mL falcon tubes for ~50 min, centrifuged for 10 s for even coverage, and then extensively washed with Millipore water until no dye was visible in rinsing water. A permanent colorant (Ion Color Brilliance Jet Black) was premixed in a 1 : 1 ratio with an Ion Sensitive Scalp 30 volume reducing agent, deposited on hair, and dyed for ~50 min. A semi-permanent colorant (Ion Color Brilliance Sky Blue) was applied on hair and after exposure for 30 minutes, the excess dye was washed with an excess of water. Same washing procedures were used for the removal of the

excess permanent dye. Microphotographs of colored hair are shown in Fig. S1.† The FTIR spectra of blue semi-permanent and black permanent hair colorants are shown in Fig. S2.†

Hair Bleaching Procedures

Hair bleach (hereafter described as 'bleach') was purchased from a local supply store (Sally's Beauty Supply LLC). Previously dyed hair and natural undyed hair were then bleached with a premixed formula of a WELLA color charm oxidizing agent and color charm powder lightener bleach in a 1.5 : 1 ratio, respectively for ~40 min. The samples were centrifuged for 10 s for even coating, and then extensively washed with Millipore water until no bleaching mix was visible in rinsing water.

Another set of the hair samples with identical dyeing procedures was independently bleached with Clorox regular concentrated liquid bleach (hereafter described as 'Clorox'), in 15 mL Falcon tubes for ~10 min. The samples were centrifuged for 10 s for even coating, and then extensively washed with Millipore water for ~3 min.

Infrared spectroscopy

FTIR spectra were acquired on a PerkinElmer 100 spectrometer equipped with an attenuated total reflectance (ATR) module. For each measurement, 4–5 pieces of hair were placed on an ATR crystal and pressed to reach 20 counts pressure (internal parameter of PerkinElmer software). Spectra were recorded with a resolution of 4 cm⁻¹ in the range of 4000–700 cm⁻¹; 15 accumulations per spectrum. A background spectrum was acquired immediately before the measurements.

Multivariate Data Analysis

PLS_Toolbox (Eigenvector Research Inc.) was used for statistical analysis of the collected Raman spectra. PLS-DA is one of the most commonly used chemometric approaches for statistical analysis of spectra collected from biological specimens.^{25–32} Spectra were mean centered. Partial least squares discriminant analysis (PLS-DA) was performed in order to determine the number of significant components and identify spectral regions that best explain the separation between the classes. In order to give each of the spectral regions equal importance, all spectra were scaled to unit variance. Raw spectra, containing wavenumbers 650–4000 cm⁻¹, were retained in the model that resulted from this iteration of PLS-DA. In total the below models were built: Model 1 (Table 2) contained 10 predictive components: LV 1 (83.48%), LV 2 (11.94%), LV 3 (1.92%), LV 4 (1.45%), LV 5 (0.58%), LV 6 (0.19%), LV 7 (0.10%), LV 8 (0.04%), LV 9 (0.02%), and LV 10 (0.04%). Model 2 (Table 3) had 6 predictive components: LV 1 (64.83%), LV 2 (22.46%), LV 3 (11.53%), LV 4 (0.35%), LV 5 (0.21%), and LV 6 (0.12%). Model 3 (Table 4) contained 6 predictive components: LV 1 (79.70%), LV 2 (13.12%), LV 3 (5.16%), LV 4 (1.33%), LV 5 (0.23%), and LV 6 (0.09%). Model 4 (Table 5) had 6 predictive components: LV 1 (82.95%), LV 2 (13.17%), LV 3 (2.45%), LV 4 (0.37%), LV 5 (0.41%), and LV 6 (0.16%). Model 5 (Table 6) had 6 predictive components: LV 1 (70.33%), LV 2 (25.75%), LV 3 (2.77%), LV 4 (0.47%), LV 5 (0.21%), and LV 6 (0.10%).

Conflicts of interest

There are no conflicts to declare.

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