

Supplementary material

Proposition of classification models for the direct evaluation of the quality of cattle and sheep leathers using laser-induced breakdown spectroscopy (LIBS) analysis

Ariane Maciel Neiva^{1,2}, Manuel Antonio Chagas Jacinto², Maurício Mello de Alencar², Sérgio Novita Esteves², Edenir Rodrigues Pereira-Filho^{1*}

¹Grupo de Análise Instrumental Aplicada (GAIA), Departamento de Química, Universidade Federal de São Carlos, São Carlos, São Paulo State, Brazil, Zip code 13565-905

²Embrapa Pecuária Sudeste, São Carlos, São Paulo State, Brazil, Zip code 13560-970

*corresponding author: erpf@ufscar.br

Phone: +55 16 3351-8092

Fax: +55 16 3351-8350

Captions for figures

Fig. S1 Plot of the average effects *versus* z values for LIBS parameter optimization using full factorial design

Fig. S2 Leather images after laser pulse

Fig. S3 Box plot graphics for 10 calculated ratios: 267/357 (1), 267/359 (2), 357/359 (3), 425/427 (4), 267/425 (5), 267/427 (6), 359/425 (7), 357/427 (8), 359/427 (9), 357/425 (10). Circle, box limits, horizontal line, error bars, and squares represents the average, standard deviation, median, 95% of confidence level, and minimum and maximum values, respectively.

Fig. S4 PC2 scores plot for the leather samples with different colors

Fig. S5 PC2 loadings plot for the leather samples with different colors

Fig. S6 PC3 scores plot for the leather samples with different colors

Fig. S7 PC3 loadings plot for the leather samples with different colors

Fig. S8 ROC curves for class 1 samples in PLS-DA calibration data set (see test identification in Table 4).

Fig. S9 ROC curves for class 2 samples in PLS-DA calibration data set (see test identification in Table 4).

Fig. S10 ROC curves for class 1 samples in PLS-DA validation data set (see test identification in Table 4).

Fig. S11 ROC curves for class 2 samples in PLS-DA validation data set (see test identification in Table 4).

Fig. S1

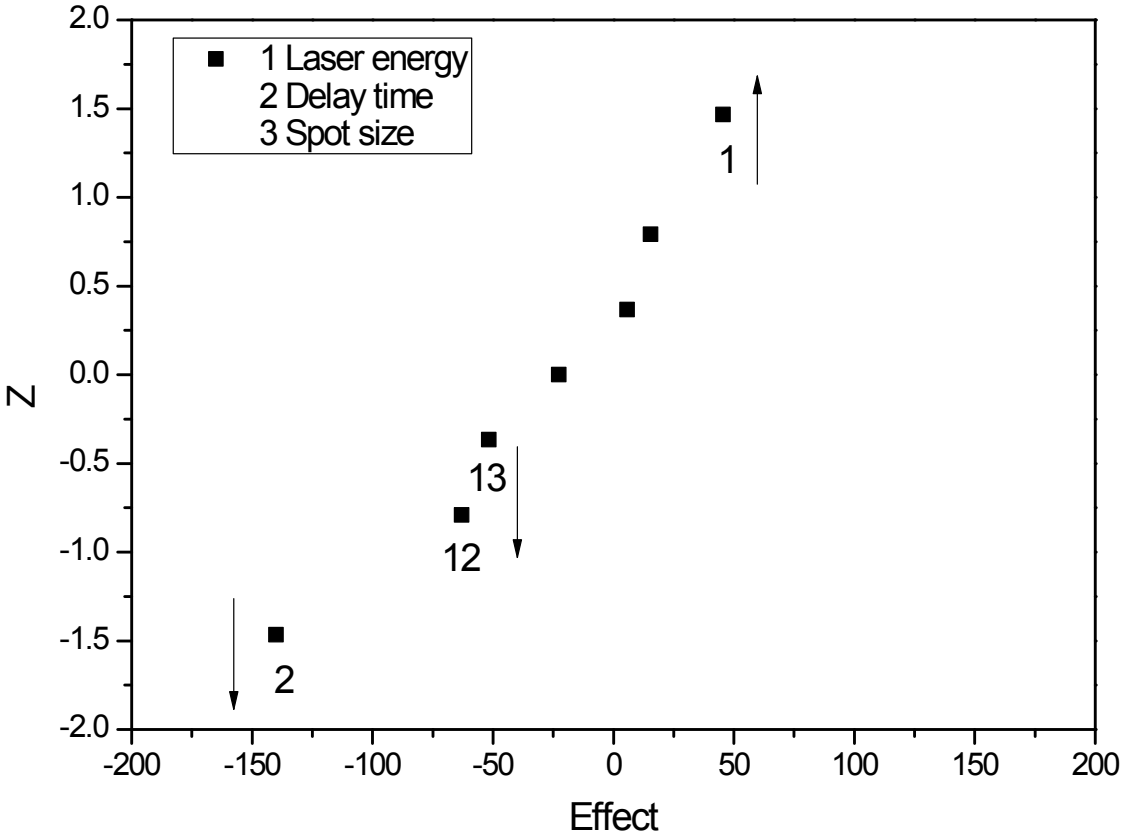


Fig. S2



Fig. S3

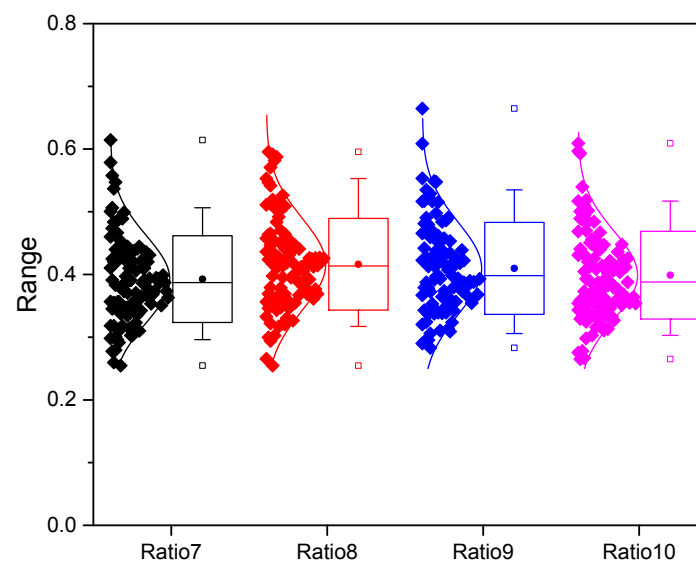
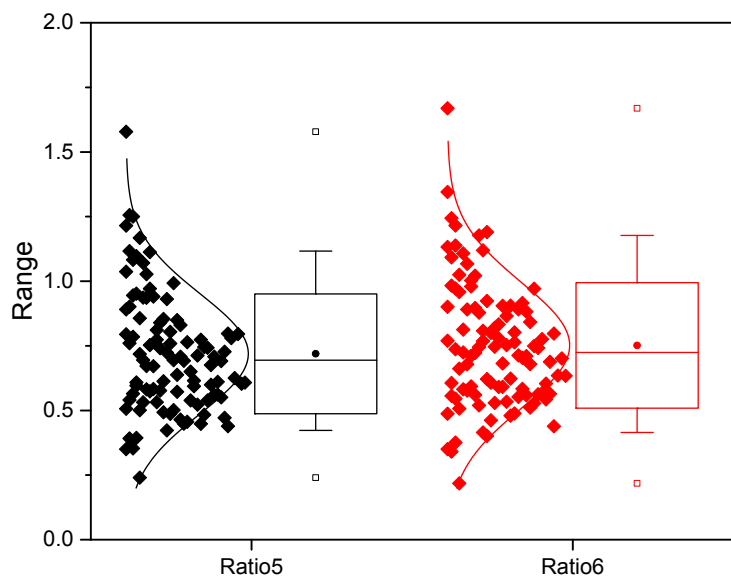
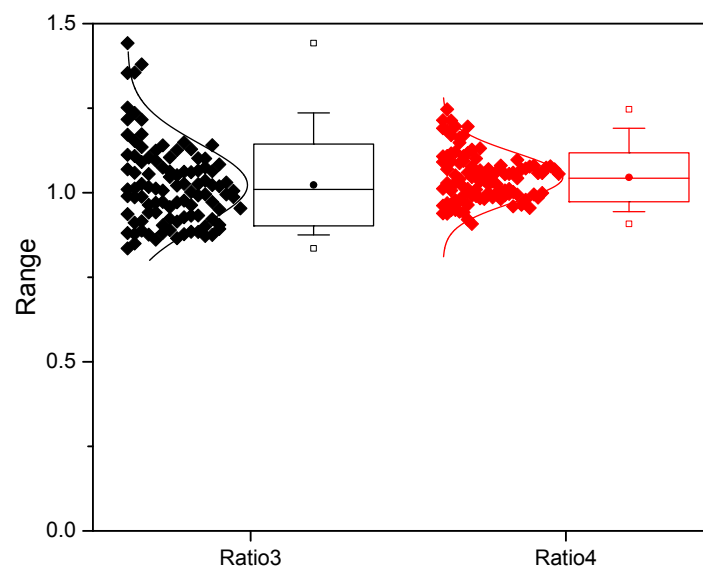
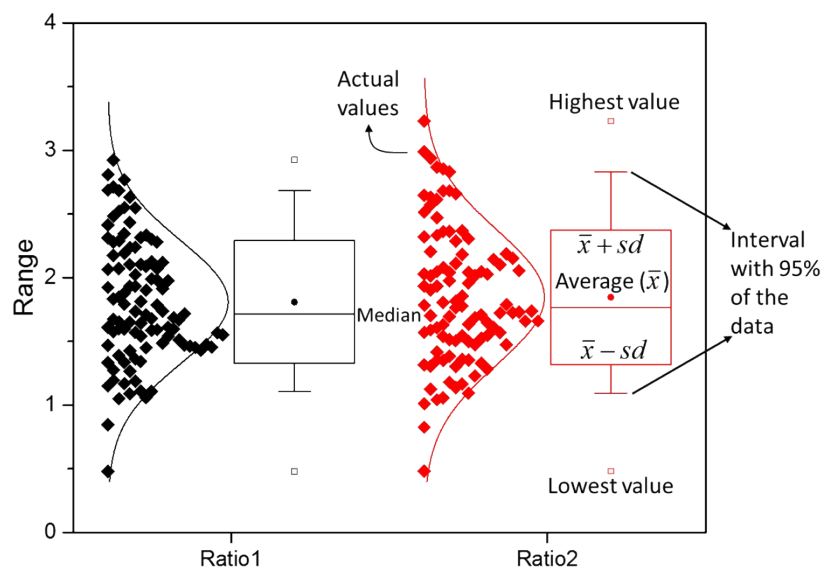


Fig. S4

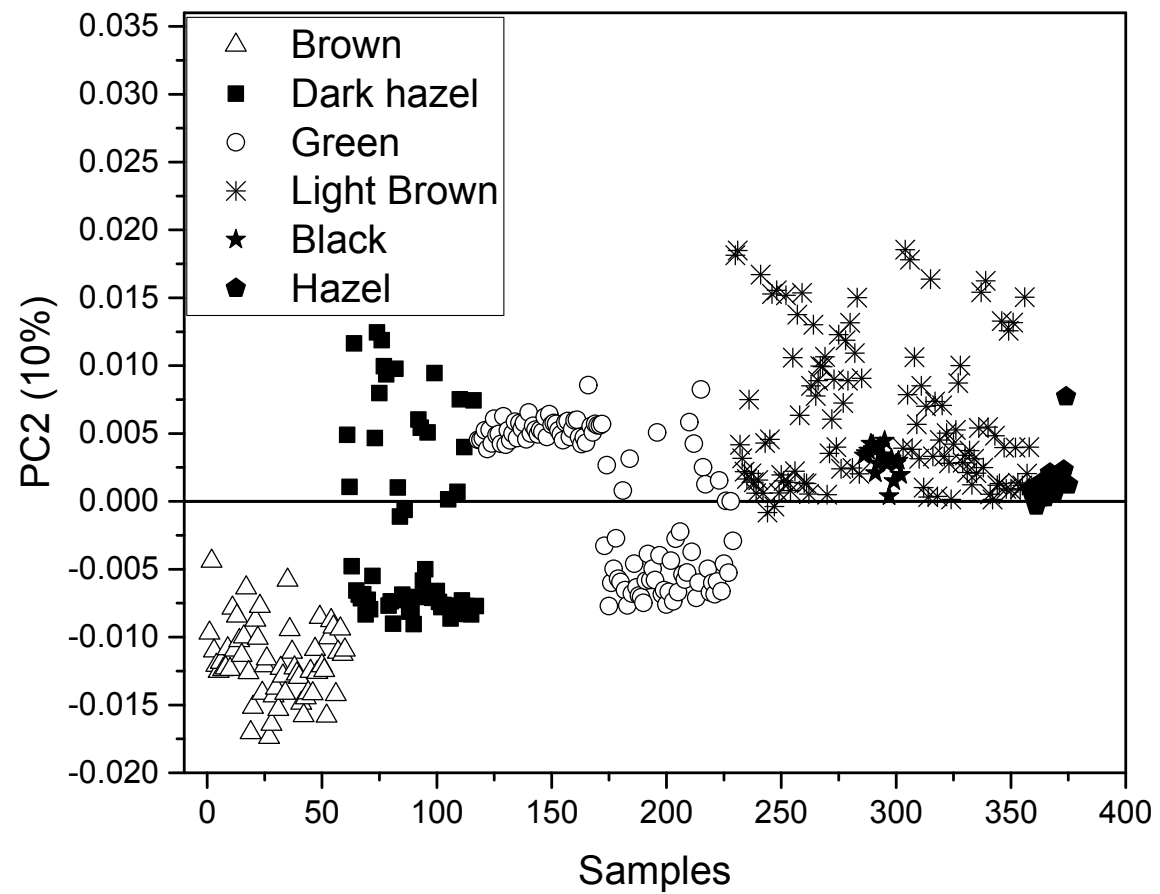


Fig. S5

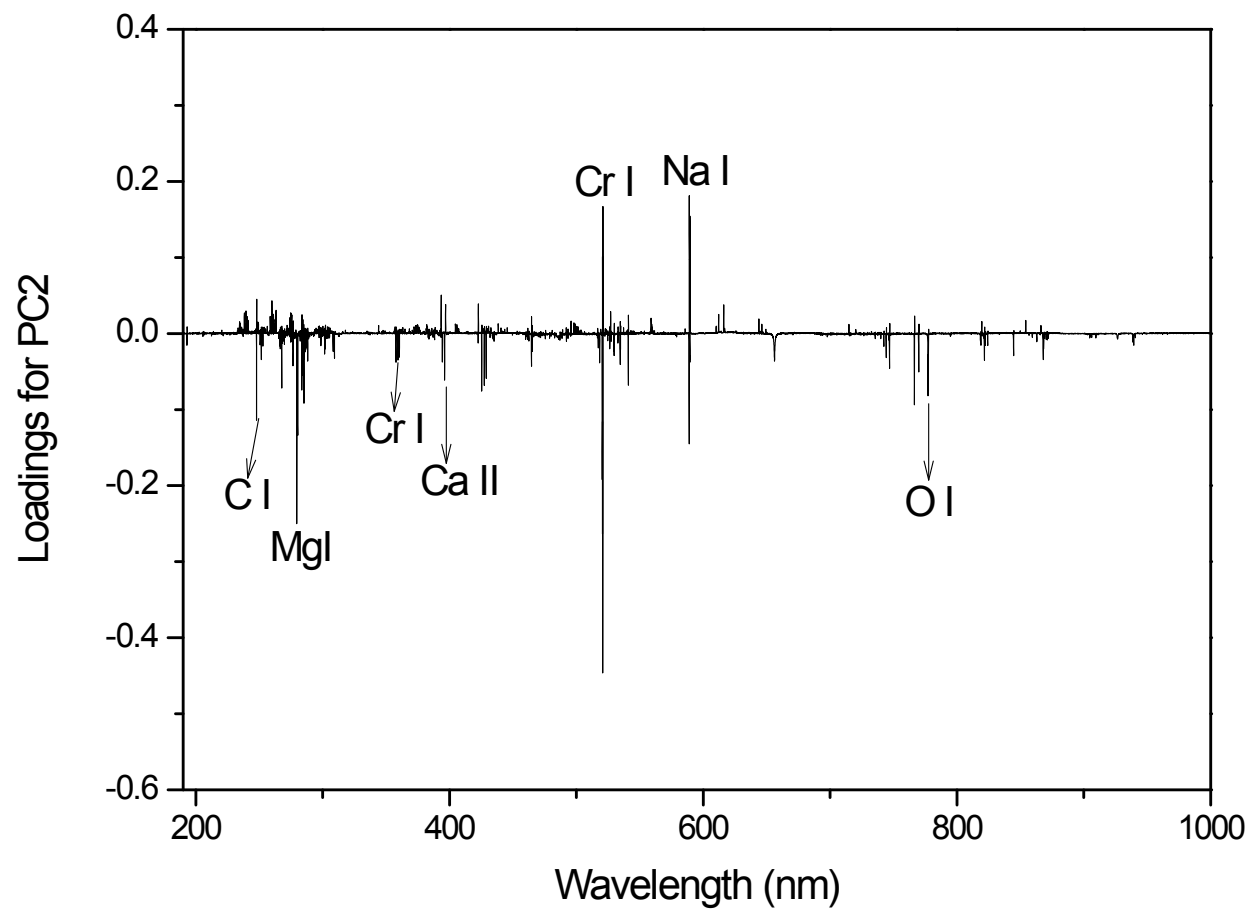


Fig. S6

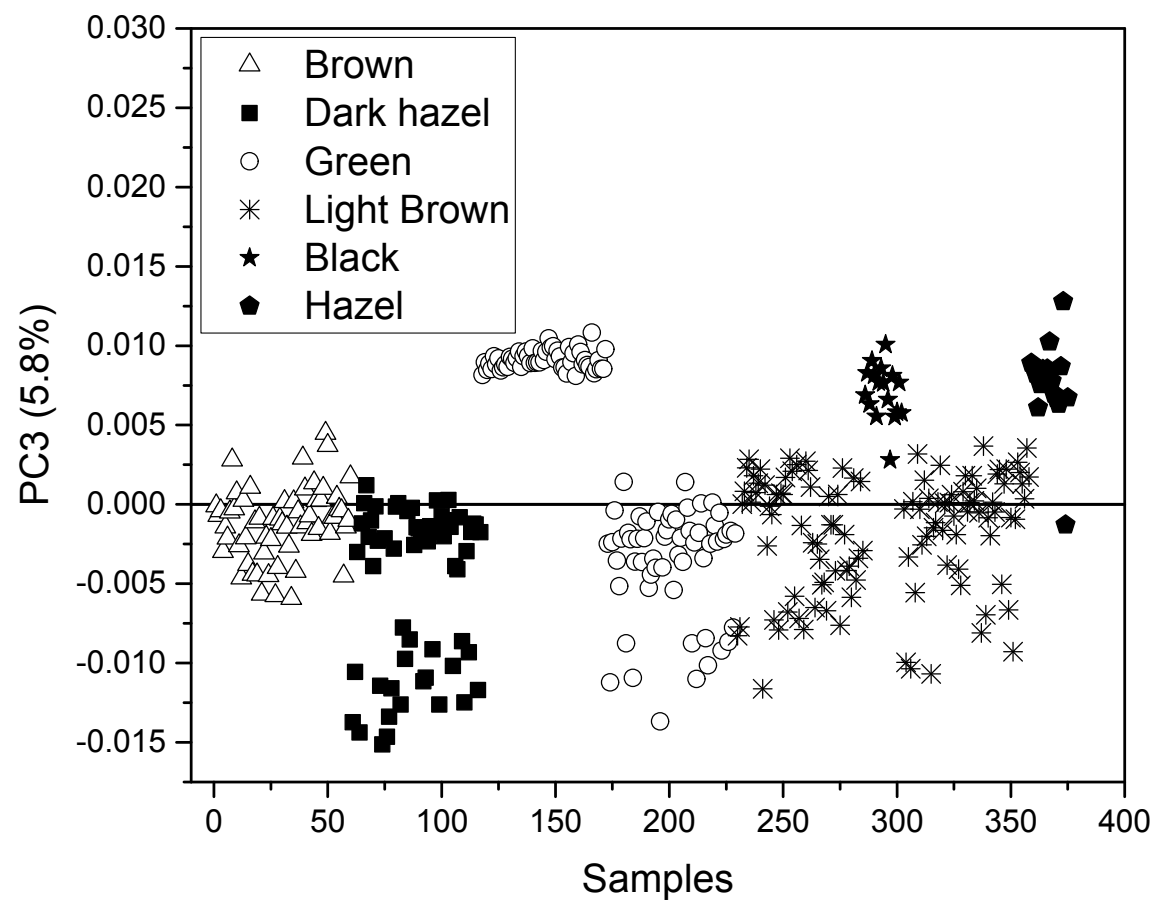


Fig. S7

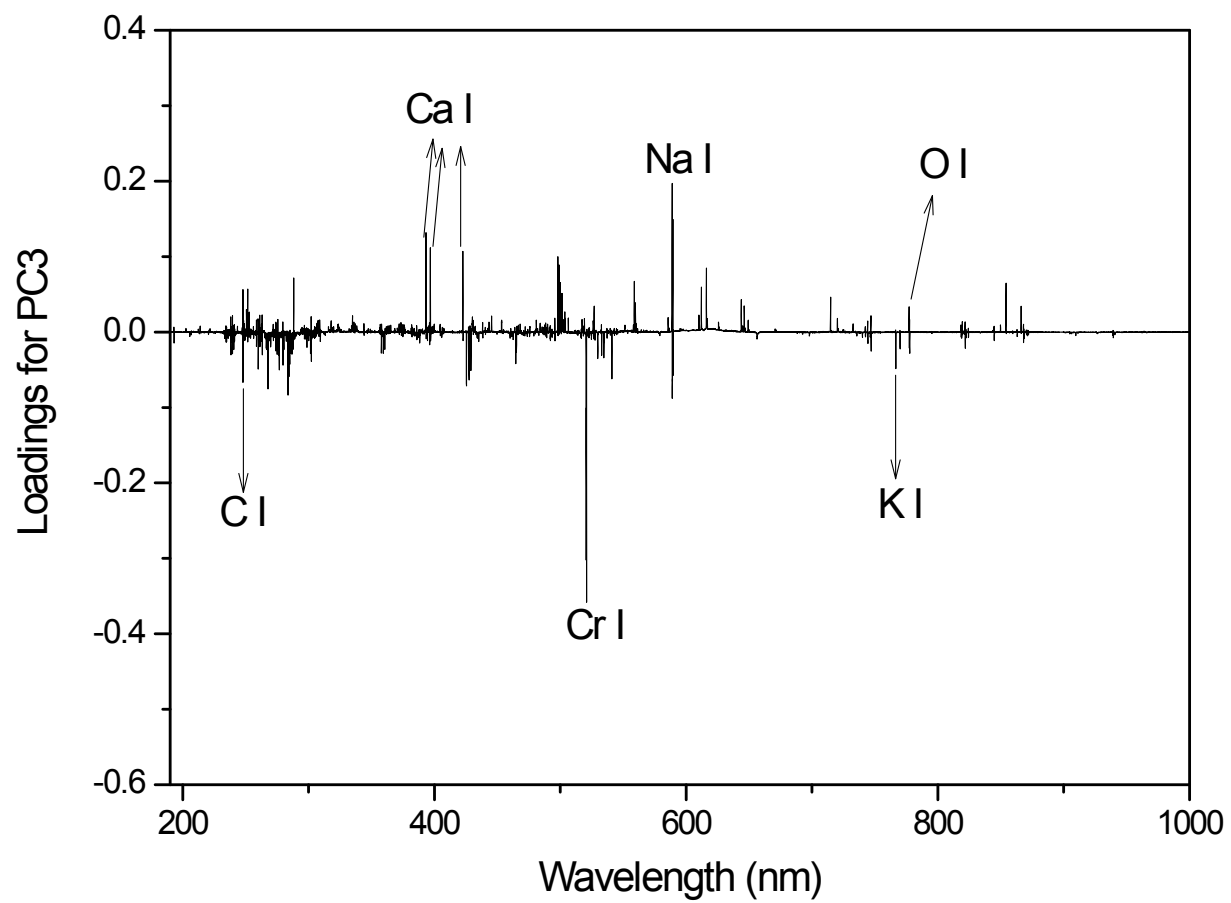


Fig. S8

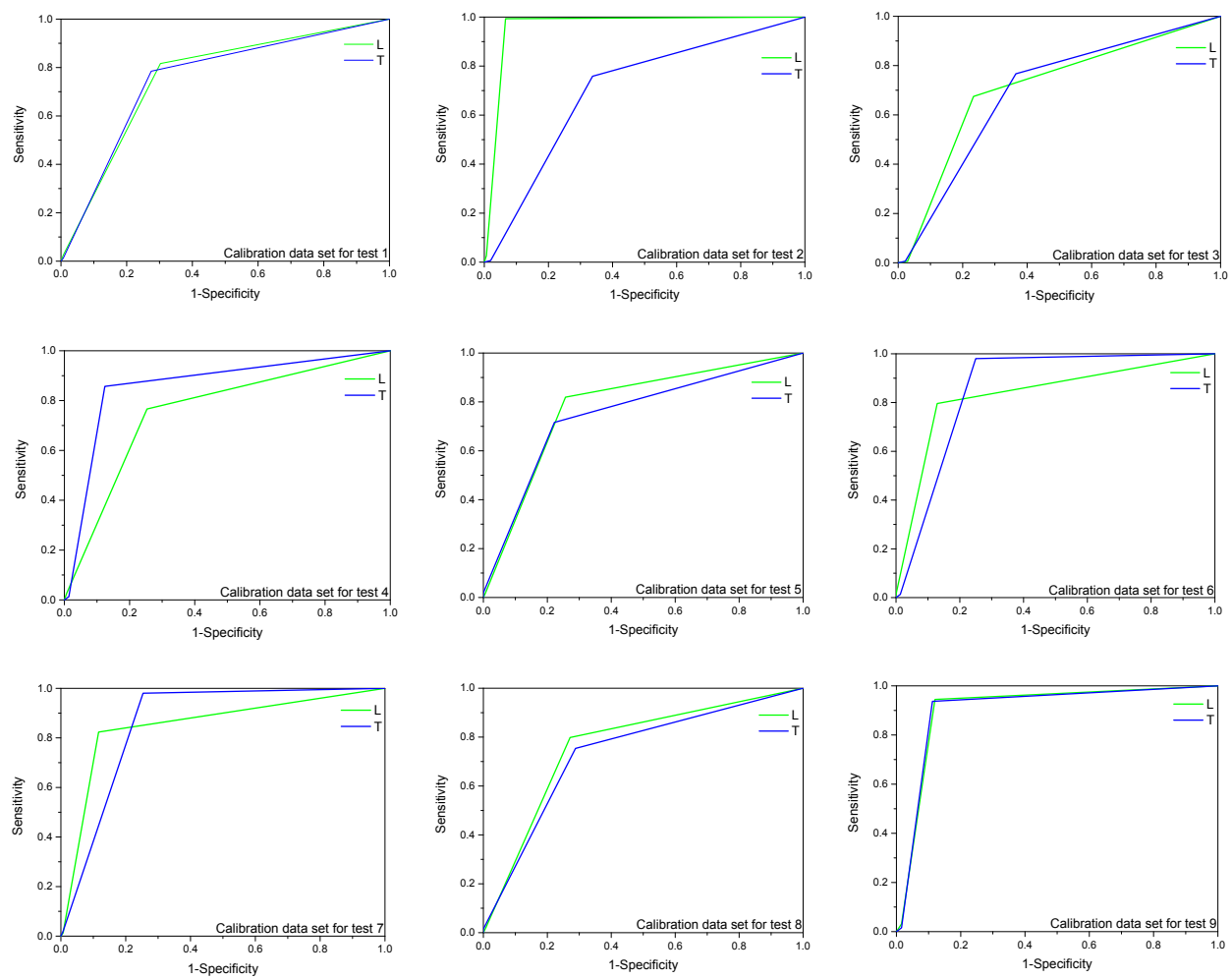


Fig. S9

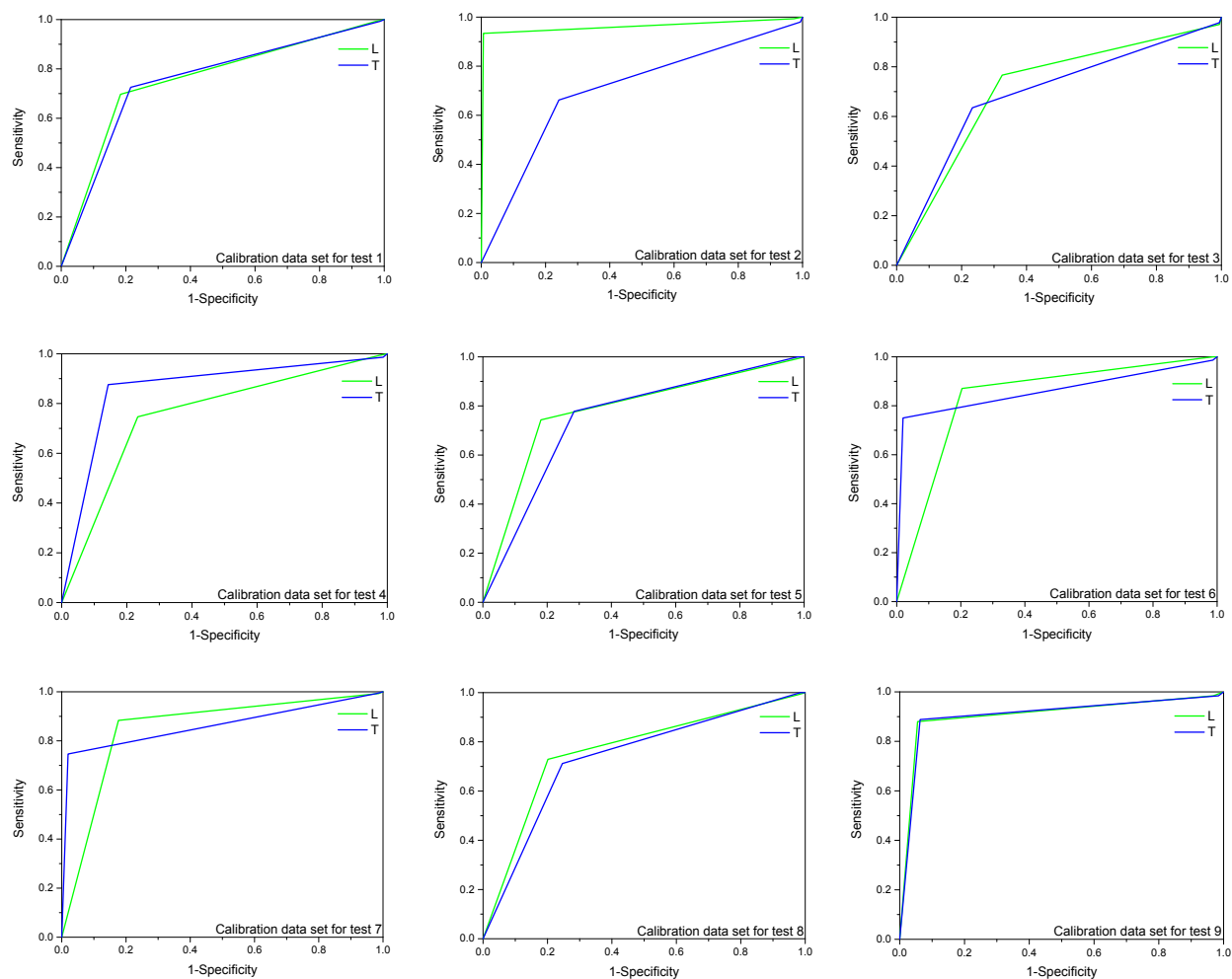


Fig. S10

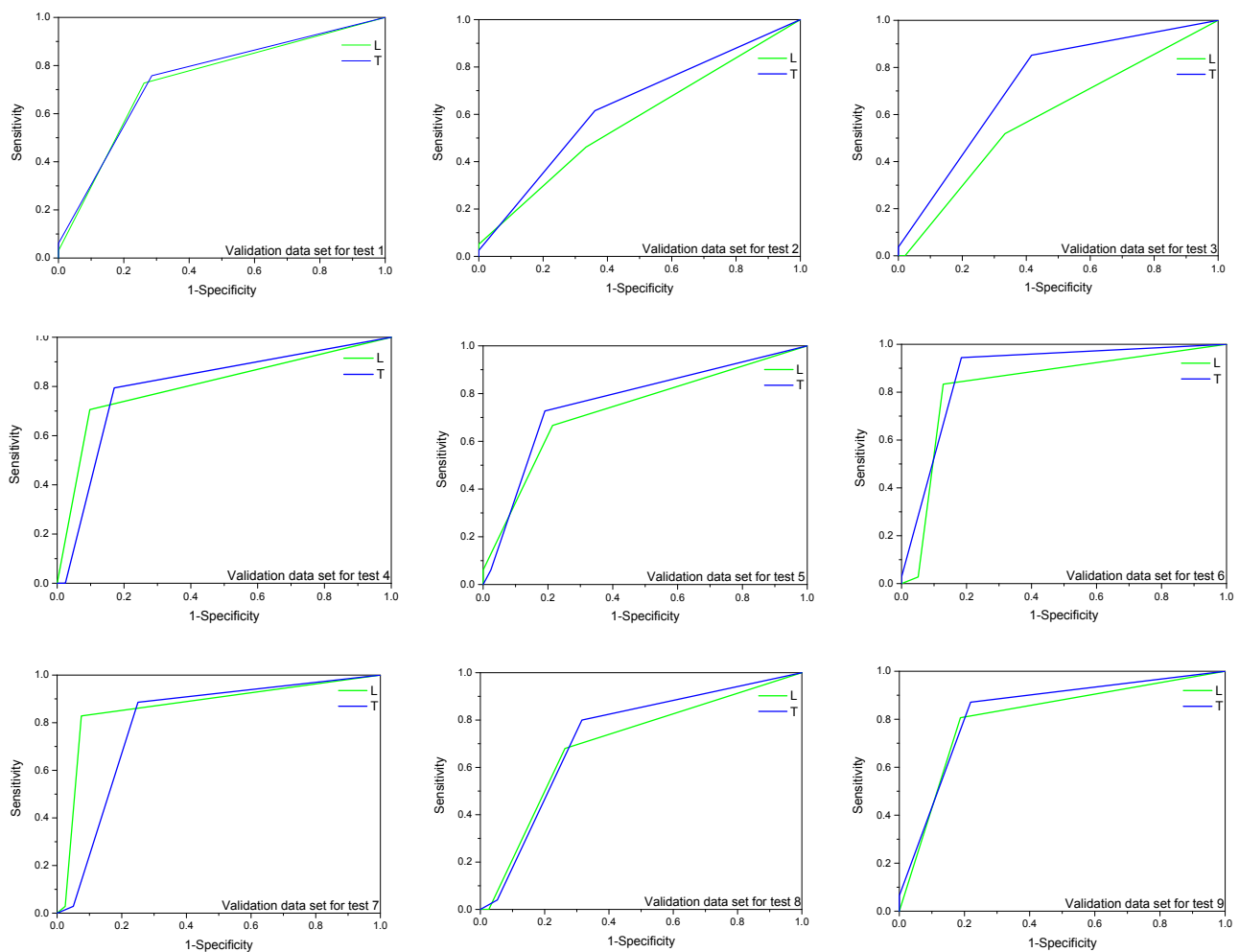
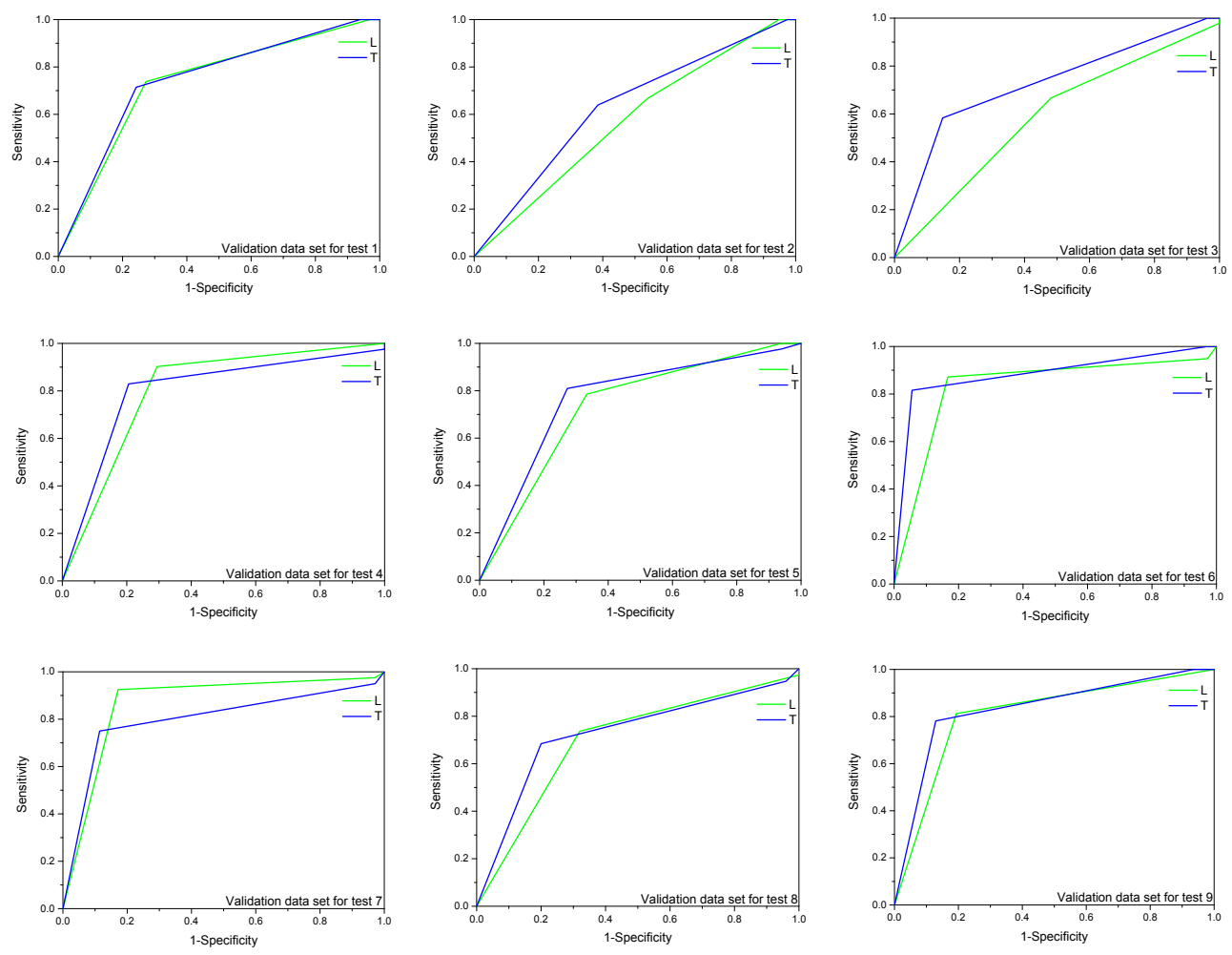


Fig. S11



Tables

Table S1 Number of samples for calibration and validation for KNN, SIMCA and PLS-DA

Test	Direction	Class 1	Class 2	All samples	Class 1	Class 2	All samples
		Calibration	Calibration	Calibration	Validation	Validation	Validation
1	L	158	142	300	33	42	75
2	L	149	151	300	39	36	75
3	L	163	137	300	27	48	75
4	L	154	146	300	34	41	75
5	L	155	144	299	33	42	75
6	L	152	147	299	36	39	75
7	L	153	146	299	35	40	75
8	L	154	118	252	25	38	63
9	L	127	125	252	31	32	63
1	T	156	144	300	34	41	75
2	T	160	140	300	29	46	75
3	T	149	151	300	39	36	75
4	T	151	148	299	37	38	75
5	T	156	143	299	32	43	75
6	T	154	146	300	33	41	74
7	T	155	144	299	33	42	75
8	T	131	121	252	25	38	63
9	T	125	127	252	33	30	63

Table S2 ANOVA table for calculated model in 359 nm

Parameter	Sum of squares	Degree of freedom	Mean square	F	F tab (95%)
Regression	1.21	6	0.201	16.9	3.58
Residue	0.0953	8	0.0119		
Total	1.30	14	0.0931		
Pure error	0.0123	2	0.00610	2.26	19.3
Lack of fit	0.0831	6	0.0138		
R ²	0.927				
R ² maximum	0.995				

Table S3 Accuracy, sensitivity, false alarm rate and specificity obtained for class 1 of SIMCA model

Test	Direction	Calibration Class 1						Validation Class 1				
		Number of samples	Number of factors	Accuracy (%)	Sensitivity (%)	False alarm rate (%)	Specificity (%)	Number of samples	Accuracy (%)	Sensitivity (%)	False alarm rate (%)	Specificity (%)
1	L	158	2	70.0	61.3	19.6	77.8	33	61.3	59.5	36.4	63.6
2	L	149	2	63.7	67.5	38.3	59.7	39	62.7	75.0	46.2	51.3
3	L	163	2	69.7	83.2	41.1	58.3	27	68.0	85.4	63.0	37.0
4	L	154	3	77.0	70.5	14.3	83.1	34	74.7	75.6	26.5	73.5
5	L	155	2	71.2	79.9	35.5	63.2	33	68.0	81.0	42.4	51.5
6	L	152	2	82.9	89.1	21.7	77.0	36	80.0	87.2	25.0	72.2
7	L	153	2	83.3	89.0	20.9	77.8	35	82.7	92.5	25.7	71.4
8	L	134	2	70.6	67.8	24.6	73.1	25	65.1	71.1	44.0	56.0
9	L	127	2	88.5	91.2	11.0	85.8	31	82.5	87.5	22.6	77.4
	Average			75.2	77.7	25.2	72.9		71.7	79.4	36.9	61.6
	Median			73.2	78.8	23.2	75.1		69.8	80.2	36.6	62.6
	SD			8.16	11.17	10.67	10.11		8.48	10.22	13.35	13.46
1	T	156	2	71.0	66.7	23.7	75.0	34	56.0	56.1	38.2	55.9
2	T	160	2	74.3	69.3	20.0	78.8	29	76.0	67.4	6.9	89.7
3	T	149	2	72.7	69.5	23.5	75.8	39	74.7	75.0	23.1	74.4
4	T	151	2	93.8	95.3	6.4	92.2	37	81.3	86.8	24.3	75.7
5	T	156	2	73.2	83.2	34.0	64.1	32	65.3	74.4	43.8	53.1
6	T	154	2	79.7	73.3	13.0	85.7	33	73.0	68.3	21.2	78.8
7	T	155	2	81.6	75.0	11.0	87.7	33	72.0	69.0	24.2	75.8
8	T	131	2	72.2	63.6	18.3	80.2	25	69.8	63.2	16.0	80.0
9	T	125	2	89.3	90.6	10.4	88.0	33	76.2	86.7	30.3	66.7
	Average			78.6	76.3	17.8	80.8		71.6	71.9	25.3	72.2
	Median			76.5	74.1	18.1	80.5		72.5	70.5	24.3	75.0
	SD			8.18	11.01	8.58	8.63		7.35	10.15	11.08	11.72

Table S4 Accuracy, sensitivity, false alarm rate and specificity obtained for class 2 of SIMCA model

Test	Direction	Calibration Class 2						Validation Class 2				
		Number of samples	Number of factors	Accuracy (%)	Sensitivity (%)	False alarm rate (%)	Specificity (%)	Number of samples	Accuracy (%)	Sensitivity (%)	False alarm rate (%)	Specificity (%)
1	L	142	2	70.0	77.8	38.0	61.3	42	61.3	63.6	40.5	59.5
2	L	151	2	63.7	59.7	31.8	67.5	36	62.7	51.3	25.0	75.0
3	L	137	2	69.7	58.3	14.6	83.2	48	68.0	37.0	12.5	85.4
4	L	146	3	77.0	83.1	28.8	70.5	41	74.7	73.5	24.4	75.6
5	L	144	2	71.2	63.2	19.4	79.9	42	68.0	51.5	19.0	81.0
6	L	147	2	82.9	77.0	10.9	89.1	39	80.0	72.2	7.7	87.2
7	L	146	2	83.3	77.8	10.3	89.0	40	82.7	71.4	5.0	92.5
8	L	118	2	70.6	73.1	31.4	67.8	38	65.1	56.0	26.3	71.1
9	L	125	2	88.5	85.8	8.0	91.2	32	82.5	77.4	12.5	87.5
	Average			75.2	72.9	21.5	77.7		71.7	61.6	19.2	79.4
	Median			73.2	75.1	20.5	78.8		69.8	62.6	19.1	80.2
	SD			8.16	10.11	11.19	11.17		8.48	13.46	11.11	10.22
1	T	144	2	71.0	75.0	32.6	66.7	41	56.0	55.9	43.9	56.1
2	T	140	2	74.3	78.8	29.3	69.3	46	76.0	89.7	32.6	67.4
3	T	151	2	72.7	75.8	28.5	69.5	36	74.7	74.4	25.0	75.0
4	T	148	2	93.8	92.2	3.4	95.3	38	81.3	75.7	10.5	86.8
5	T	143	2	73.2	64.1	16.8	83.2	43	65.3	53.1	23.3	74.4
6	T	146	2	79.7	85.7	25.3	73.3	41	73.0	78.8	29.3	68.3
7	T	144	2	81.6	87.7	24.3	75.0	42	72.0	75.8	26.2	69.0
8	T	121	2	72.2	80.2	36.4	63.6	38	69.8	80.0	31.6	63.2
9	T	127	2	89.3	88.0	7.9	90.6	30	76.2	66.7	13.3	86.7
	Average			78.6	80.8	22.7	76.3		71.6	72.2	26.2	71.9
	Median			76.5	80.5	24.8	74.1		72.5	75.0	26.2	70.5
	SD			8.18	8.63	11.18	11.01		7.35	11.72	10.09	10.15

Table S5 Accuracy, sensitivity, false alarm rate and specificity obtained for class 1 of PLS-DA model

Test	Direction	Calibration Class 1						Validation Class 1				
		Number of samples	Number of factors	Accuracy (%)	Sensitivity (%)	False alarm rate (%)	Specificity (%)	Number of samples	Accuracy (%)	Sensitivity (%)	False alarm rate (%)	Specificity (%)
1	L	158	3	74.7	69.7	18.4	79.1	33	72.0	71.4	24.2	72.7
2	L	149	3	95.0	93.4	0.7	96.6	39	53.3	66.7	53.8	41.0
3	L	163	3	71.3	76.6	32.5	66.9	27	61.3	66.7	48.1	51.9
4	L	154	3	74.3	74.7	23.4	74.0	34	81.3	90.2	29.4	70.6
5	L	155	3	77.3	74.3	18.1	80.0	33	70.7	78.6	33.3	60.6
6	L	152	3	82.6	87.1	20.4	78.3	36	84.0	87.2	16.7	80.6
7	L	153	3	84.6	88.4	17.6	81.0	35	86.7	92.5	17.1	80.0
8	L	134	3	75.4	72.9	20.1	77.6	25	71.4	73.7	32.0	68.0
9	L	127	2	89.7	88.0	5.5	91.3	31	90.5	87.5	6.5	93.5
	Average			80.5	80.6	17.4	80.5		74.6	79.4	29.0	68.8
	Median			78.9	78.6	18.2	79.6		73.3	79.0	29.2	69.7
	SD			7.97	8.58	9.38	8.81		12.21	10.23	15.15	15.89
1	T	156	3	74.3	71.5	21.8	76.9	34	72.0	73.2	23.5	70.6
2	T	160	3	71.3	68.6	25.0	73.8	29	80.0	71.7	3.4	93.1
3	T	149	3	71.7	63.6	19.5	79.9	39	76.0	72.2	17.9	79.5
4	T	151	3	89.6	90.5	9.9	88.7	37	82.7	86.8	21.6	78.4
5	T	156	3	84.4	78.3	12.4	86.8	32	73.3	79.1	28.1	65.6
6	T	154	3	82.7	71.9	5.8	92.9	33	78.4	75.6	15.2	81.8
7	T	155	3	83.9	72.9	4.5	94.2	33	74.7	71.4	18.2	78.8
8	T	131	3	72.2	70.2	24.4	74.0	25	68.3	65.8	24.0	72.0
9	T	125	2	89.7	87.4	6.4	92.0	33	85.7	86.7	6.1	84.8
	Average			80.0	75.0	14.4	84.4		76.8	75.8	17.6	78.3
	Median			81.3	72.4	13.4	85.6		76.4	74.4	18.1	78.6
	SD			7.63	8.85	8.31	8.27		5.48	7.13	8.24	8.18

Table S6 Accuracy, sensitivity, false alarm rate and specificity obtained for class 2 of PLS-DA model

Test	Direction	Calibration Class 2						Validation Class 2				
		Number of samples	Number of factors	Accuracy (%)	Sensitivity (%)	False alarm rate (%)	Specificity (%)	Number of samples	Accuracy (%)	Sensitivity (%)	False alarm rate (%)	Specificity (%)
1	L	142	3	74.7	79.1	29.6	69.7	42	72.0	72.7	28.6	71.4
2	L	151	3	95.0	96.6	6.0	93.4	36	53.3	41.0	33.3	66.7
3	L	137	3	71.3	66.9	20.4	76.6	48	61.3	51.9	31.3	66.7
4	L	146	3	74.3	74.0	24.7	74.7	41	81.3	70.6	9.8	90.2
5	L	144	3	77.3	80.0	25.0	74.3	42	70.7	60.6	21.4	78.6
6	L	147	3	82.6	78.3	12.9	87.1	39	84.0	80.6	7.7	87.2
7	L	146	3	84.6	81.0	11.0	88.4	40	86.7	80.0	5.0	92.5
8	L	118	3	75.4	77.6	26.3	72.9	38	71.4	68.0	23.7	73.7
9	L	125	2	89.7	91.3	10.4	88.0	32	90.5	93.5	12.5	87.5
	Average			80.5	80.5	18.5	80.6		74.6	68.8	19.2	79.4
	Median			78.9	79.6	19.5	78.6		73.3	69.7	20.3	79.0
	SD			7.97	8.81	8.50	8.58		12.21	15.89	10.76	10.23
1	T	144	3	74.3	76.9	27.8	71.5	41	72.0	70.6	26.8	73.2
2	T	140	3	71.3	73.8	30.0	68.6	46	80.0	93.1	28.3	71.7
3	T	151	3	71.7	79.9	34.4	63.6	36	76.0	79.5	27.8	72.2
4	T	148	3	89.6	88.7	8.1	90.5	38	82.7	78.4	10.5	86.8
5	T	143	3	84.4	86.8	21.7	78.3	43	73.3	65.6	18.6	79.1
6	T	146	3	82.7	92.9	26.7	71.9	41	78.4	81.8	19.5	75.6
7	T	144	3	83.9	94.2	25.7	72.9	42	74.7	78.8	23.8	71.4
8	T	121	3	72.2	74.0	29.8	70.2	38	68.3	72.0	28.9	65.8
9	T	127	2	89.7	92.0	11.0	87.4	30	85.7	84.8	13.3	86.7
	Average			80.0	84.4	23.9	75.0		76.8	78.3	22.0	75.8
	Median			81.3	85.6	26.2	72.4		76.4	78.6	22.9	74.4
	SD			7.63	8.27	8.87	8.85		5.48	8.18	6.82	7.13