Electronic Supplementary Material (ESI) for Analytical Methods.

Supplementary information

Direct chemical inspection of eye shadow and lipstick solid samples using laser-induced breakdown spectroscopy (LIBS) and chemometrics: proposition of classification models

Amanda dos Santos Augusto, Érica Ferreira Batista and Edenir Rodrigues Pereira-Filho*

Federal University of São Carlos, Chemistry Department, Group of Applied Instrumental Analysis, P.O. Box 676, Zip Code 13565-905, São Carlos – São Paulo State, Brazil.

**Corresponding author: erpf@ufscar.br*

Phone: +55 16 3351-8092

Fax: +55 16 3351-8350

Table 1S Emission lines for ICP OES determination.

Analytes	Emission lines (nm)
Cd	228.8(I)
Co	228.6(II)
Cr	283.5(II)/357.8(I)
Cu	224.7(II)/324.7(I)
Ni	231.6(II)/341.4(I)

*Atomic (I) or ionic (II) lines

Table 2S 2^3 Full factorial design, central point (11 experiments) and averaged norm.

Experiment	Laser energy		Spot size		Delay time		Average norm (n = 25)
	Coded level	Real (mJ)	Coded level	Real (μm)	Coded level	Real (μs)	
1	0	75	0	150	0	1	4,941
2	0	75	0	150	0	1	7,056
3	0	75	0	150	0	1	4,320
4	-1	50	-1	50	-1	0.5	7,309
5	1	100	-1	50	-1	0.5	21,646
6	-1	50	1	250	-1	0.5	1,138
7	1	100	1	250	-1	0.5	9,000
8	-1	50	-1	150	1	1.5	1,497
9	1	100	-1	50	1	1.5	7,930
10	-1	50	1	250	1	1.5	516
11	1	100	1	250	1	1.5	1,473

Table 3S Effects and percentage values of the variables (1 = laser energy, 2 = spot size and 3 = delay time) and its interactions (12, 13, 23 and 123).

Variables and interaction effects	Calculated effect values	Percentage of each effect
3 (delay time)	-6,919	27
2 (spot size)	-6,564	24
13	-3,702	8
12	-2,988	5
123	250	0
23	2,845	5
1 (laser energy)	7,398	31

Table 4S: RSD values description for eyeshadow samples

Emission line	Signal type	Average RSD	RSD range		Emission line	Signal type	Average RSD	RSD range	
			Lower	Higher				Lower	Higher
1: C I	Area	23	7	49	19: Mg II	Area	36	18	50
(193.091)	Height	23	7	50	(293.651)	Height	37	18	50
2: Si I	Area	30	12	50	20: Ti II	Area	36	13	49
(212.412)	Height	31	13	50	(306.622)	Height	36	14	50
3: Si I	Area	29	10	50	21: Ti II	Area	38	19	50
(221.667)	Height	30	10	50	(307.297)	Height	36	17	50
4: Fe II	Area	35	15	50	22: Ti II	Area	38	19	50
(234.349)	Height	35	15	50	(307.522)	Height	36	17	50
5: C I	Area	24	7	49	23: Ti II	Area	38	20	50
(247.856)	Height	25	8	49	(307.864)	Height	38	16	50
6: Fe II	Area	38	16	50	24: Ti II	Area	38	18	50
(274.320)	Height	36	12	50	(308.802)	Height	38	17	50
7: Fe II	Area	37	12	50	25: Ti I	Area	38	22	50
(274.648)	Height	35	13	50	(334.188)	Height	37	17	50
8: Fe II	Area	37	12	50	26: Ti II	Area	37	19	50
(274.948)	Height	35	13	50	(334.904)	Height	37	19	50
9: Fe I	Area	-	-	-	27: Ti II	Area	36	19	50
(275.403)	Height	35	17	50	(336.121)	Height	37	19	49
10: Fe II	Area	35	15	50	28: Ti II	Area	37	21	50
(275.573)	Height	35	14	50	(337.280)	Height	37	19	50
11: Mg I	Area	35	15	49	29: Ti II	Area	38	20	50
(277.983)	Height	36	15	50	(338.376)	Height	37	20	50
12: Mg II	Area	36	15	50	30: Ca II	Area	36	19	50
(279.078)	Height	36	15	49	(393.366)	Height	35	16	50
13: Mg II	Area	25	4	50	31: Ca II	Area	36	17	50
(279.533)	Height	24	3	49	(396.847)	Height	35	18	49
14: Mg II	Area	-	-	-	32: Na I	Area	26	5	49
(279.799)	Height	31	7	50	(588.995)	Height	24	0	50
15: Mg II	Area	28	5	50	33: Na I	Area	26	5	49
(280.270)	Height	24	2	49	(589.593)	Height	24	0	50
16: Mg I	Area	32	9	49	35: Li I	Area	32	14	50
(285.213)	Height	33	10	50	(670.776)	Height	31	13	49
17: Si I	Area	32	12	50	39: K I	Area	29	11	49
(288.157)	Height	32	12	50	(766.490)	Height	28	8	50
18: Mg II	Area	37	18	49	40: K I	Area	30	11	49
(292.863)	Height	37	19	50	(769.896)	Height	29	9	50
					42: Ba II	Area	41	21	50
					(493.409)	Height	38	20	50

Table 5S: RSD values description for lipstick samples

Emission line	Signal type	Average RSD	RSD range		Emission line	Signal type	Average RSD	RSD range	
			Lower	Higher				Lower	Higher
1: C I	Area	18	7	27	19: Mg II	Area	32	25	43
(193.091)	Height	18	7	28	(293.651)	Height	39	24	50
2: Si I	Area	29	27	30	20: Ti II	Area	37	22	49
(212.412)	Height	33	17	50	(306.622)	Height	38	21	50
3: Si I	Area	41	35	48	21: Ti II	Area	39	20	50
(221.667)	Height	37	21	46	(307.297)	Height	39	20	49
4: Fe II	Area	31	19	48	22: Ti II	Area	39	20	50
(234.349)	Height	33	19	49	(307.522)	Height	39	20	49
5: C I	Area	18	7	31	23: Ti II	Area	39	22	49
(247.856)	Height	18	9	31	(307.864)	Height	40	21	50
6: Fe II	Area	37	22	49	24: Ti II	Area	39	24	50
(274.320)	Height	36	20	50	(308.802)	Height	39	23	50
7: Fe II	Area	34	34	34	25: Ti I	Area	39	25	50
(274.648)	Height	34	18	49	(334.188)	Height	36	18	50
8: Fe II	Area	34	34	34	26: Ti II	Area	38	19	50
(274.948)	Height	34	18	49	(334.904)	Height	39	19	50
9: Fe I	Area	-	-	-	27: Ti II	Area	38	23	49
(275.403)	Height	34	17	50	(336.121)	Height	38	22	49
10: Fe II	Area	32	18	48	28: Ti II	Area	39	21	49
(275.573)	Height	34	17	50	(337.280)	Height	39	19	49
11: Mg I	Area	40	29	49	29: Ti II	Area	41	22	50
(277.983)	Height	37	22	50	(338.376)	Height	39	20	50
12: Mg II	Area	-	-	-	30: Ca II	Area	40	28	48
(279.078)	Height	37	17	48	(393.366)	Height	36	25	47
13: Mg II	Area	46	42	49	31: Ca II	Area	40	31	49
(279.533)	Height	42	29	48	(396.847)	Height	38	26	49
14: Mg II	Area	-	-	-	32: Na I	Area	36	19	49
(279.799)	Height	43	36	50	(588.995)	Height	35	22	50
15: Mg II	Area	44	40	50	33: Na I	Area	36	19	49
(280.270)	Height	43	36	47	(589.593)	Height	35	22	50
16: Mg I	Area	43	36	47	35: Li I	Area	40	19	48
(285.213)	Height	41	25	50	(670.776)	Height	34	20	49
17: Si I	Area	46	42	49	39: K I	Area	34	15	49
(288.157)	Height	42	26	50	(766.490)	Height	34	14	50
18: Mg II	Area	-	-	-	40: K I	Area	37	17	49
(292.863)	Height	38	23	50	(769.896)	Height	35	15	47
					42: Ba II	Area	40	21	47
					(493.409)	Height	37	20	47

Spectra obtained for experiments 1, 5, 7 and 10 of the 2^3 full factorial design presented at Table 3.

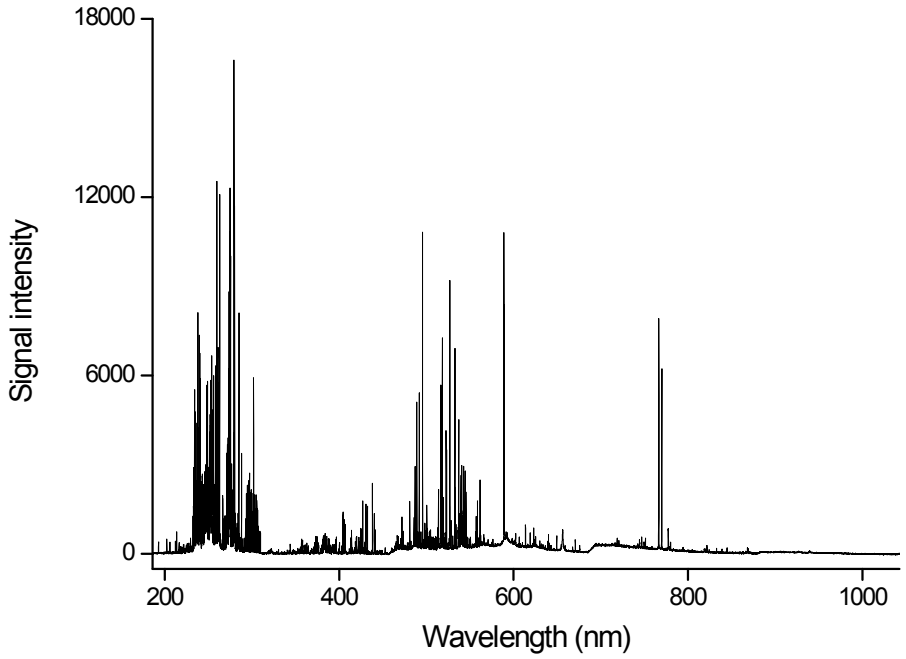


Figure 1S – Emission spectrum obtained for eye shadow sample with the experimental conditions (75 mJ, 150 μm and 1 μs) described in Experiment 1 (see Table 2S).

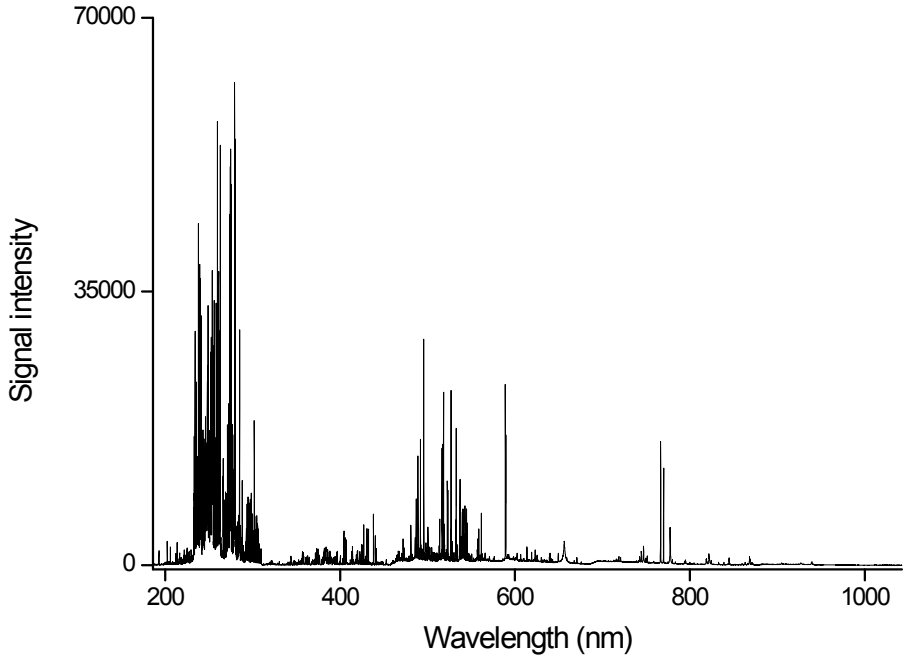


Figure 2S – Emission spectrum obtained for eye shadow sample with the experimental conditions (100 mJ, 50 μm and 0.5 μs) described in Experiment 5 (see Table 2S).

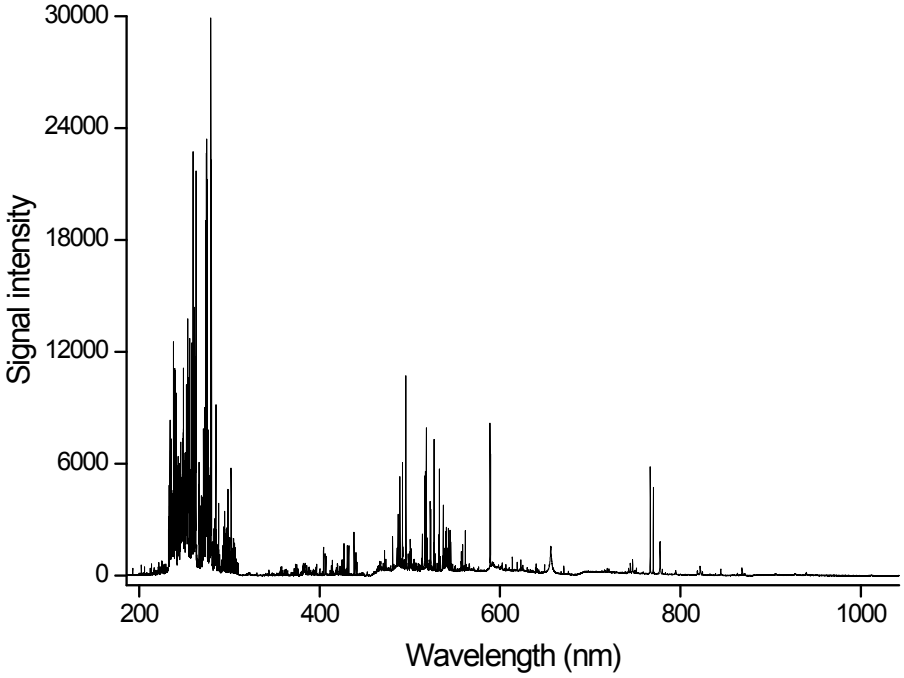


Figure 3S – Emission spectrum obtained for eye shadow sample with the experimental conditions (100 mJ, 250 μm and 0.5 μs) described in Experiment 7 (see Table 2S).

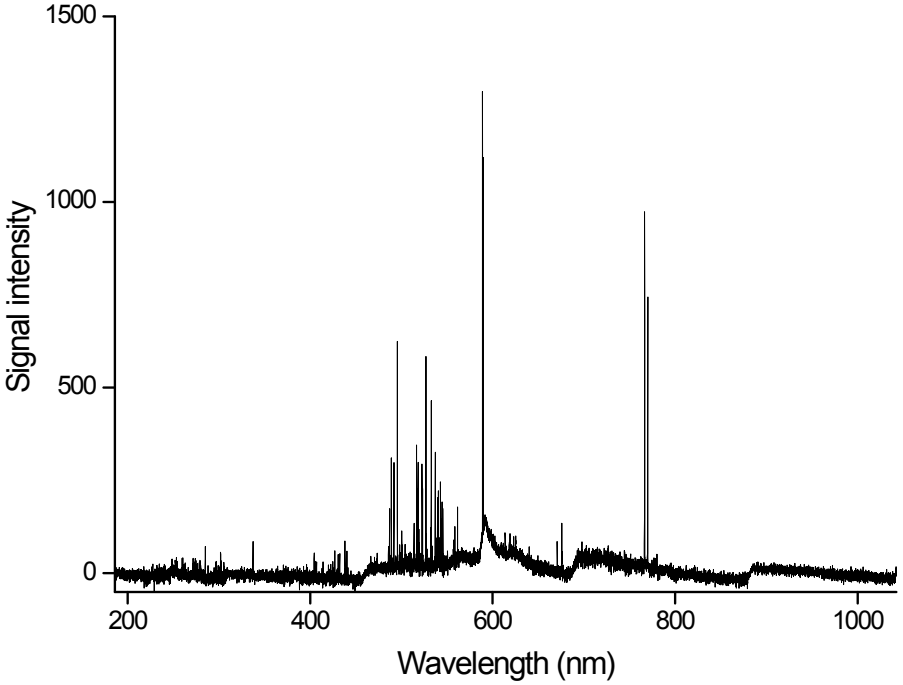
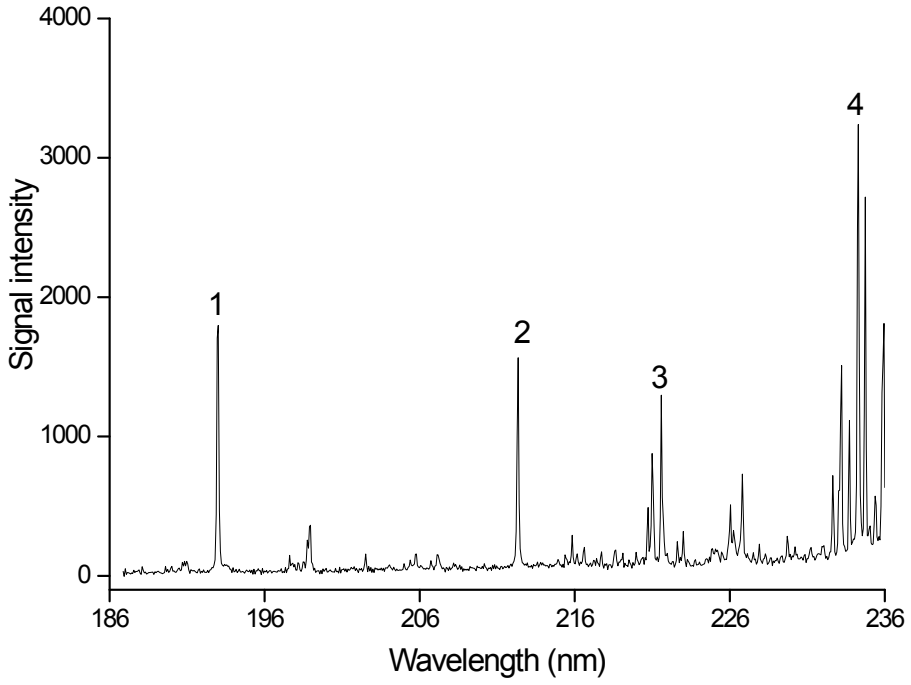


Figure 4S – Emission spectrum obtained for eye shadow sample with the experimental conditions (50 mJ, 250 μm and 1.5 μs) described in Experiment 10 (see Table 2S).

Emission spectra fragments for eye shadow sample.



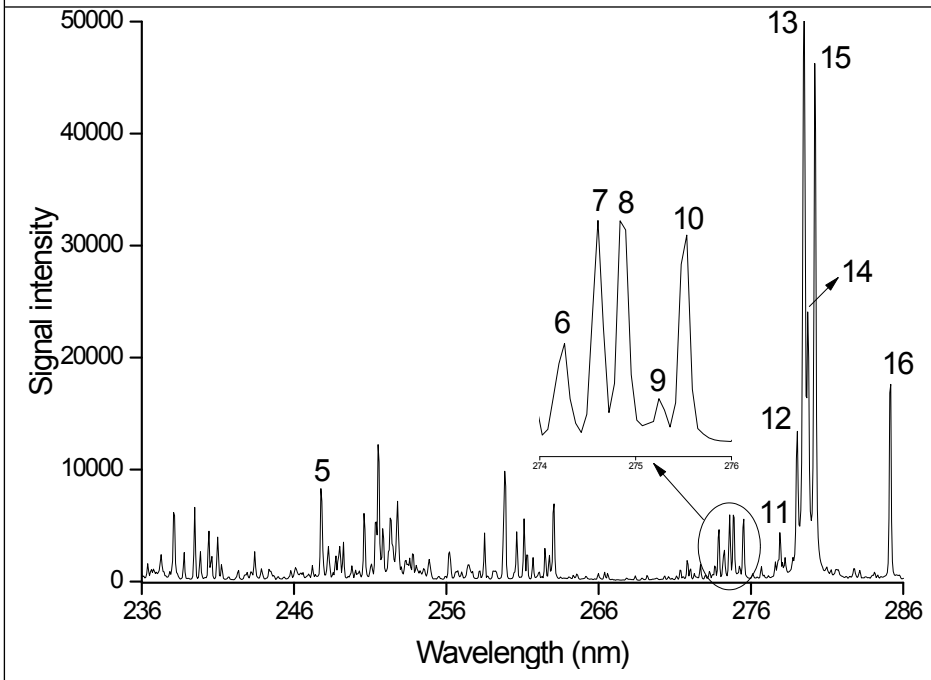
1: C I (193.091)

2: Si I (212.412)

3: Si I (221.667)

4: Fe II (234.349)

Figure 5S: Emission spectrum from 186 to 236 nm for eye shadow sample.



5: C I (247.856)

6: Fe II (274.320)

7: Fe II (274.648)

8: Fe II (274.948)

9: Fe I (275.403)

10: Fe II (275.573)

11: Mg I (277.983)

12: Mg II (279.078)

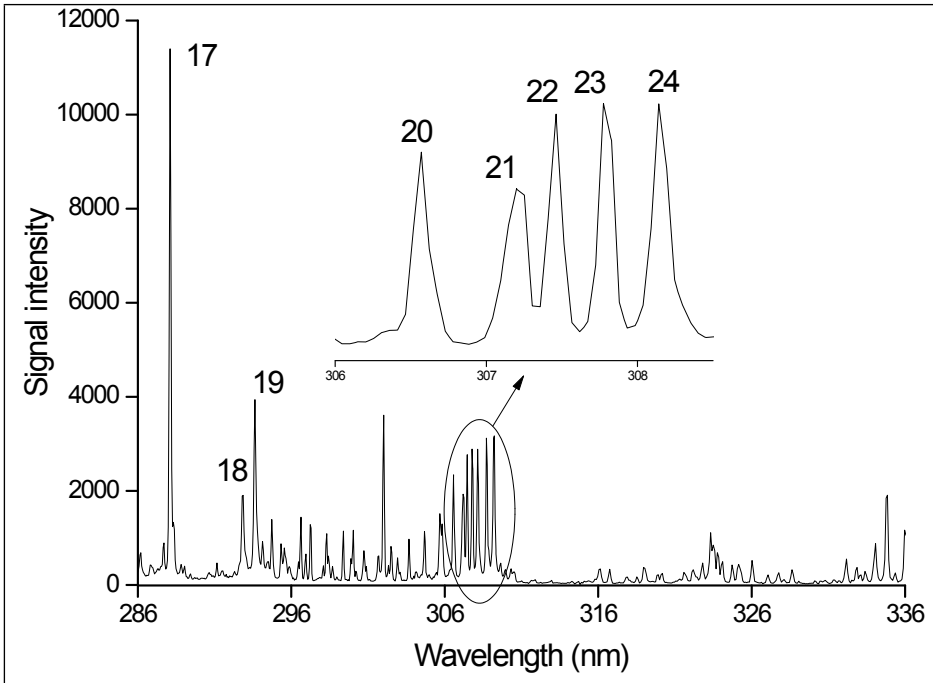
13: Mg II (279.533)

14: Mg II (279.799)

15: Mg II (280.270)

16: Mg I (285.213)

Figure 6S: Emission spectrum from 236 to 286 nm for eye shadow sample.



17: Si I (288.157)

18: Mg II (292.863)

19: Mg II (293.651)

20: Ti II (306.622)

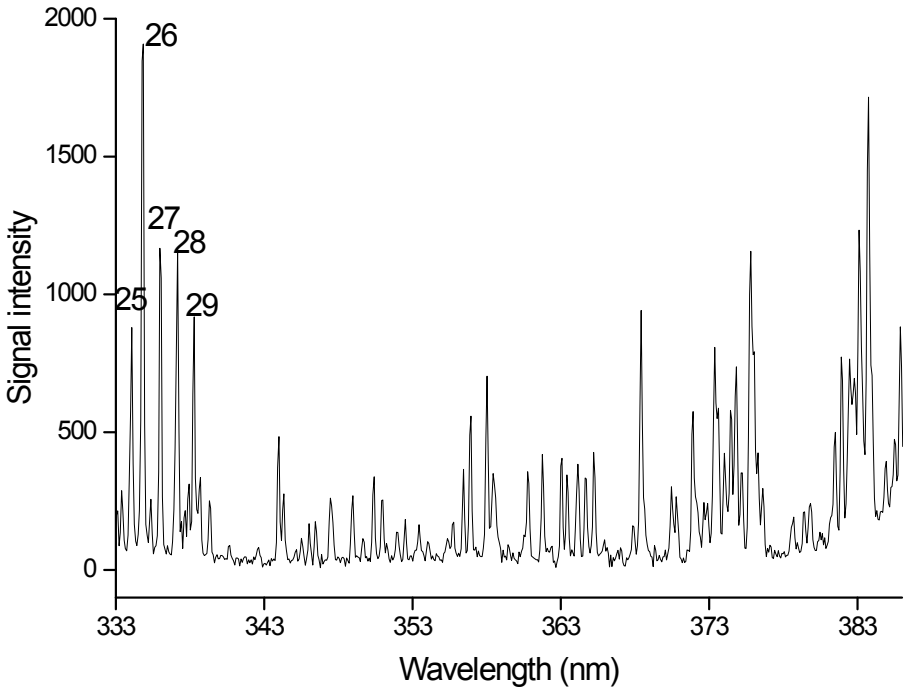
21: Ti II (307.297)

22: Ti II (307.522)

23: Ti II (307.864)

24: Ti II (308.802)

Figure 7S: Emission spectrum from 286 to 336 nm for eye shadow sample.



25: Ti I (334.188)

26: Ti II (334.904)

27: Ti II (336.121)

28: Ti II (337.280)

29: Ti II (338.376)

Figure 8S: Emission spectrum from 333 to 386 nm for eye shadow sample.

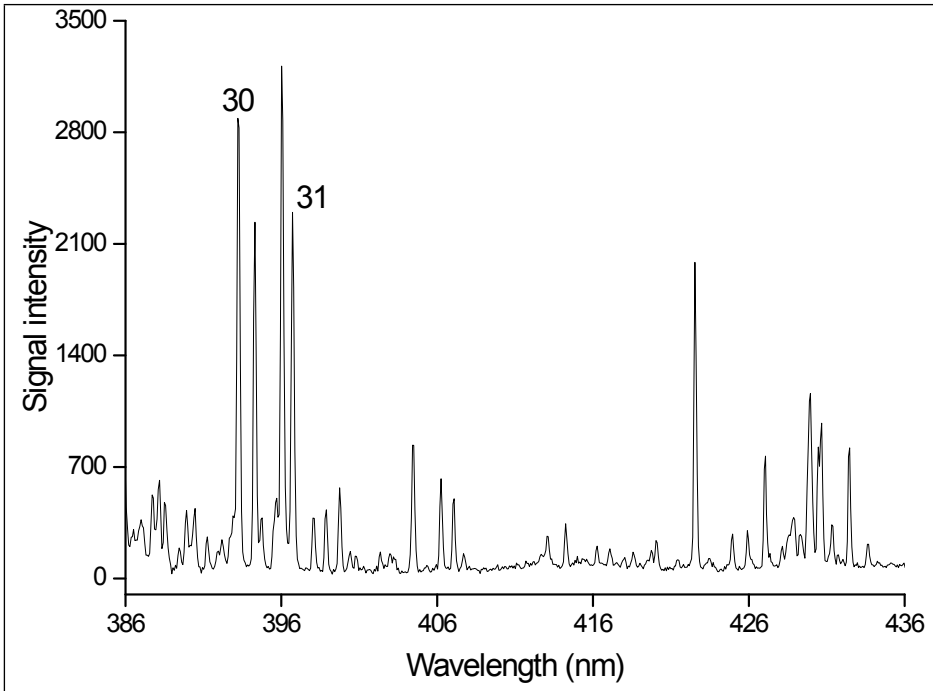


Figure 9S: Emission spectrum from 386 to 436 nm for eye shadow sample.

30: Ca II (393.366)

31: Ca II (396.847)

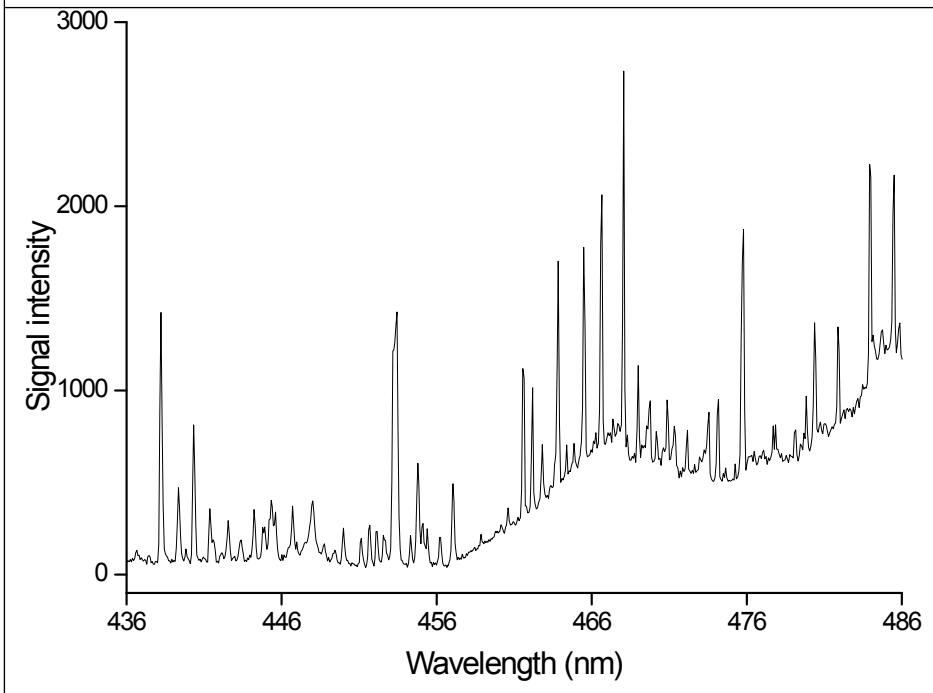


Figure 10S: Emission spectrum from 436 to 486 nm for eye shadow sample.

Around 20 emission lines for Ti

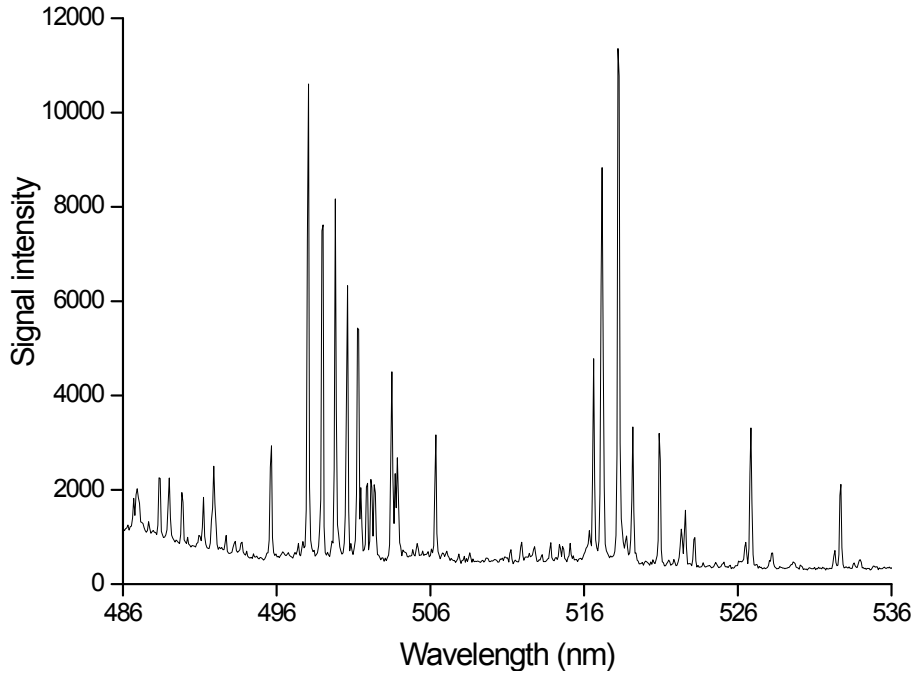


Figure 11S: Emission spectrum from 486 to 536 nm for eye shadow sample.

Twenty emission lines for Ti and 4 emission lines for Mg.

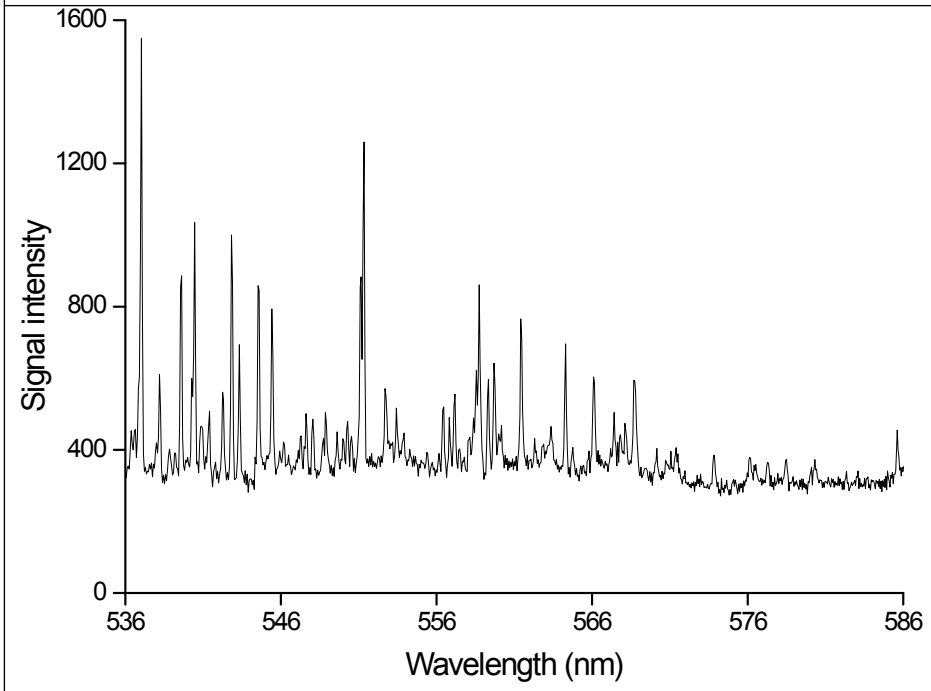


Figure 12S: Emission spectrum from 536 to 586 nm for eye shadow sample.

Around 20 emission lines for Ti and Fe

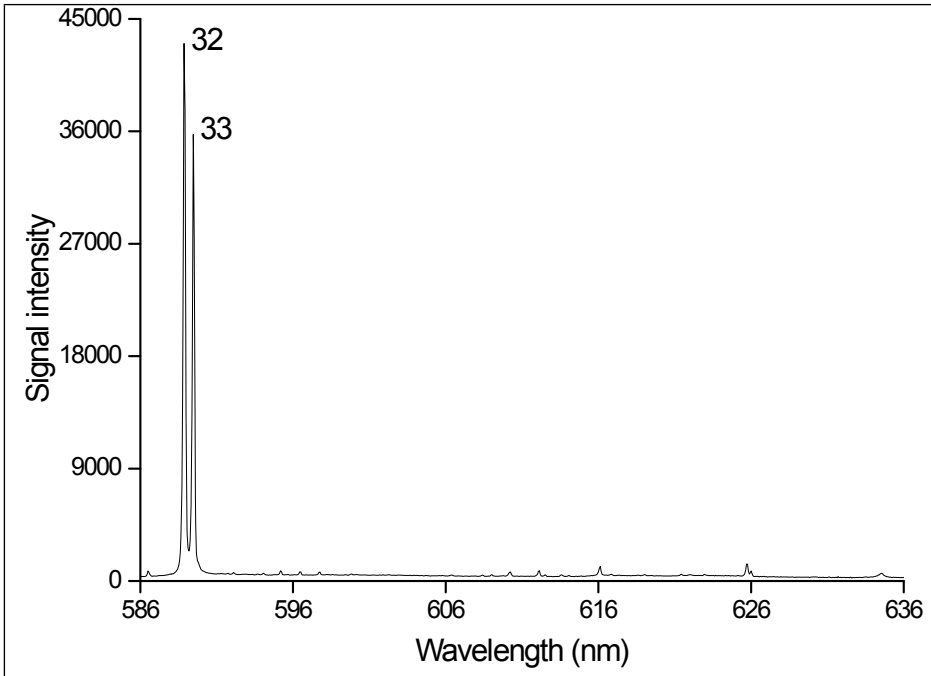


Figure 13S: Emission spectrum from 586 to 636 nm for eye shadow sample.

32: Na I (588.995)

33: Na I (589.593)

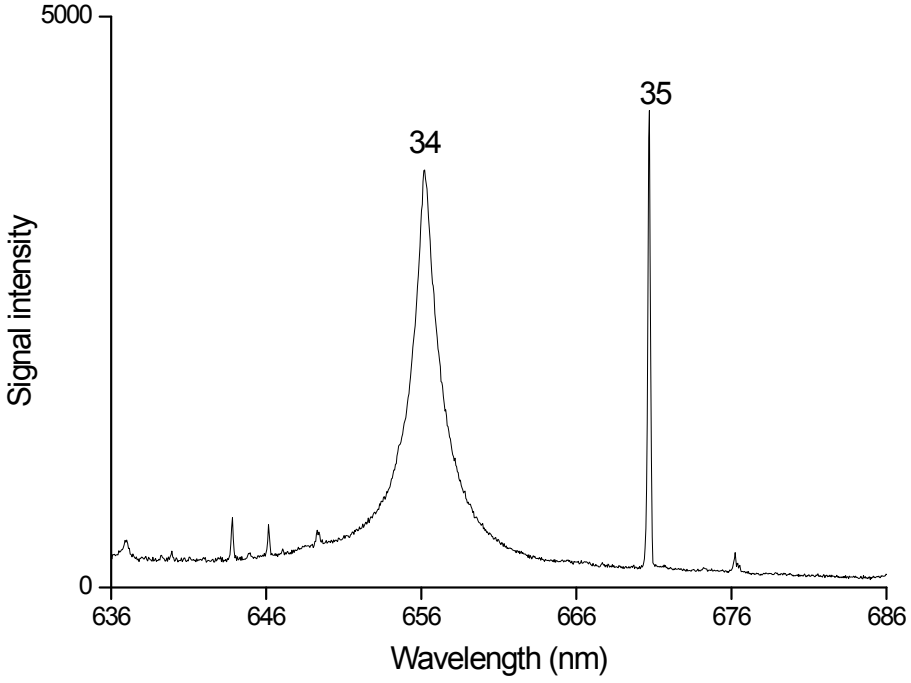


Figure 14S: Emission spectrum from 636 to 686 nm for eye shadow sample.

34: H I (656.286)

35: Li I (670.776)

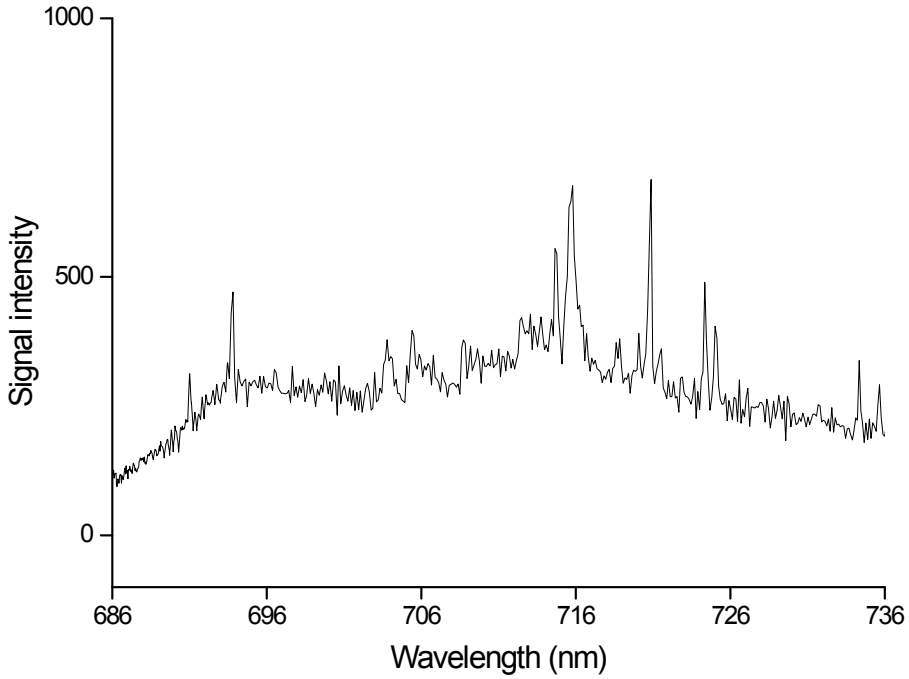


Figure 15S: Emission spectrum from 686 to 736 nm for eye shadow sample.

No emission line was identified

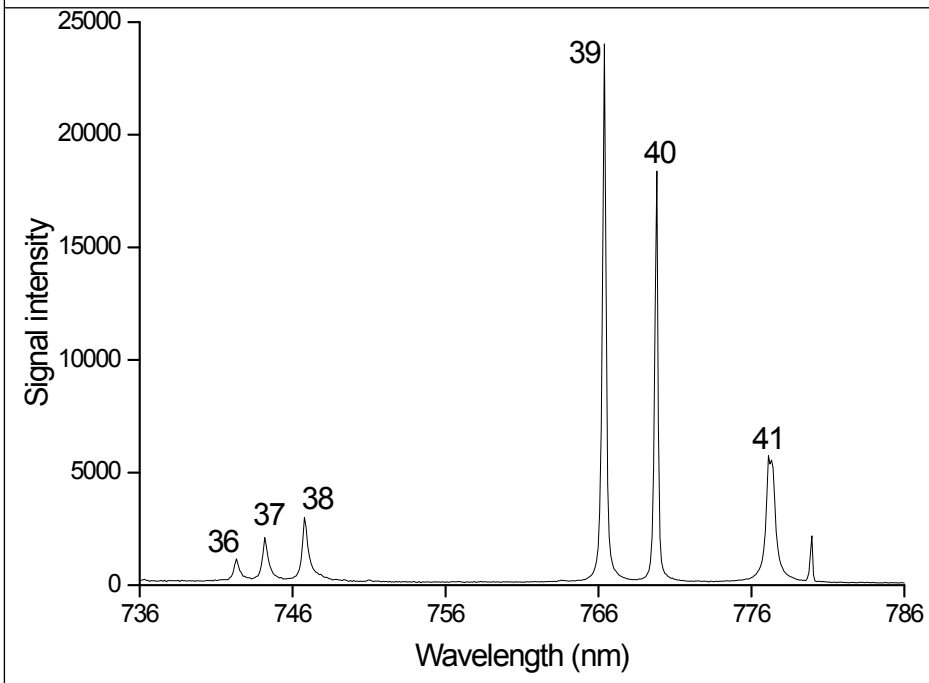


Figure 16S: Emission spectrum from 736 to 786 nm for eye shadow sample.

36: N I (742.368)

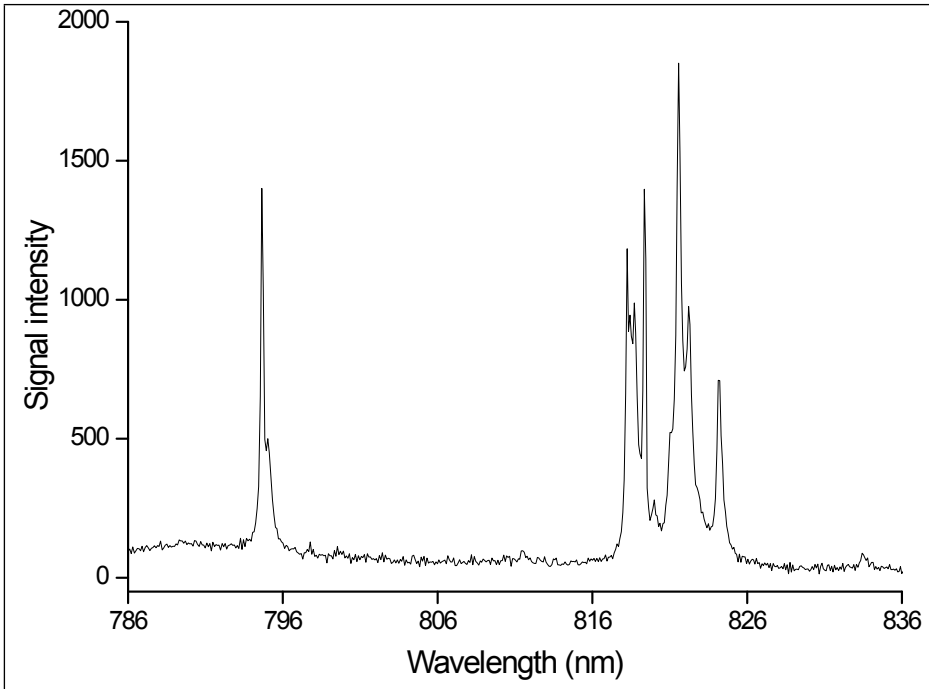
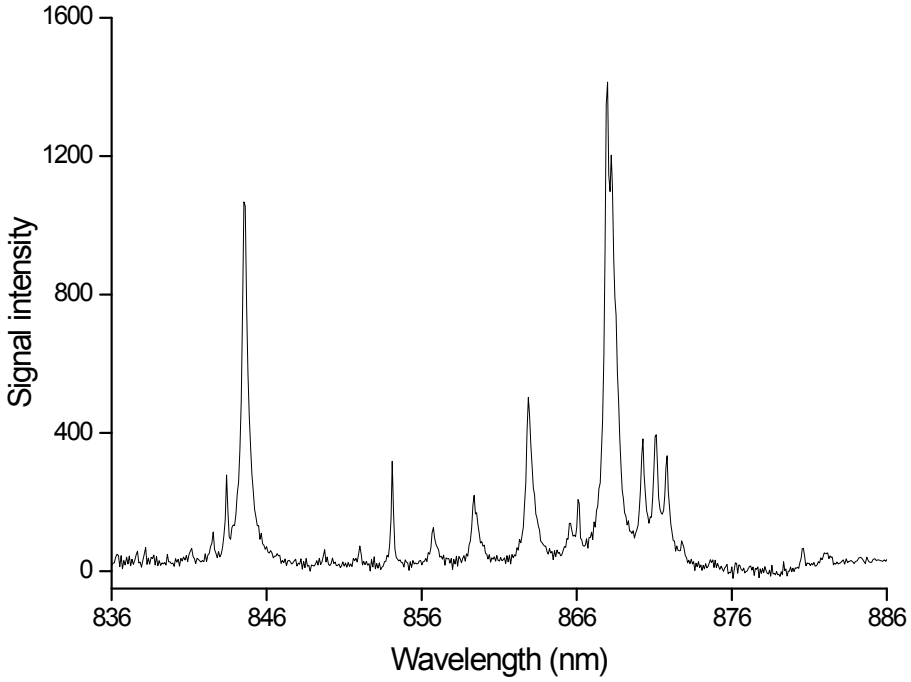
37: N I (744.230)

38: N I (746.831)

39: K I (766.490)

40: K I (769.896)

41: O I (777.421)

 **Figure 17S**: Emission spectrum from 786 to 836 nm for eye shadow sample.	Several O and N (7 lines) emission lines
 **Figure 18S**: Emission spectrum from 836 to 886 nm for eye shadow sample.	Several O and N (16 lines) emission lines

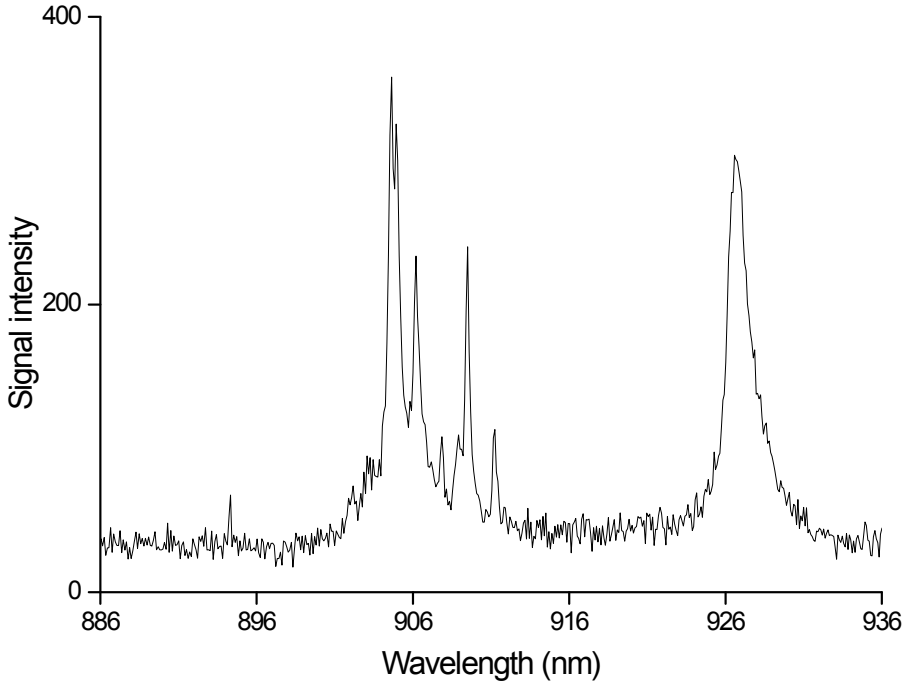


Figure 19S: Emission spectrum from 886 to 936 nm for eye shadow sample.

No emission lines were identified

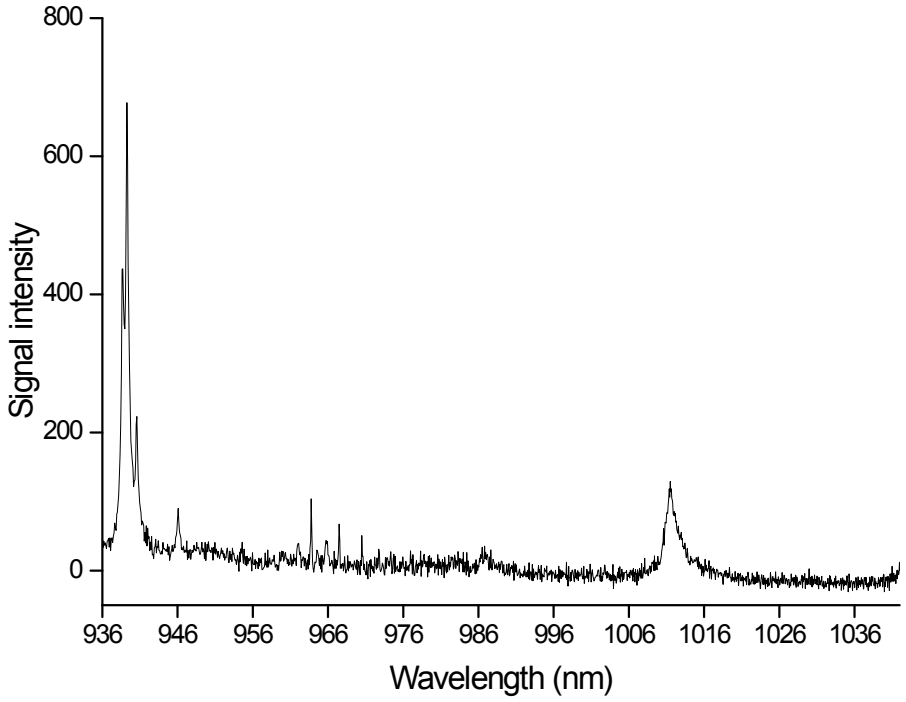


Figure 20S: Emission spectrum from 936 to 1042 nm for eye shadow sample.

No emission lines were identified

Emission spectra fragments for lipstick sample.

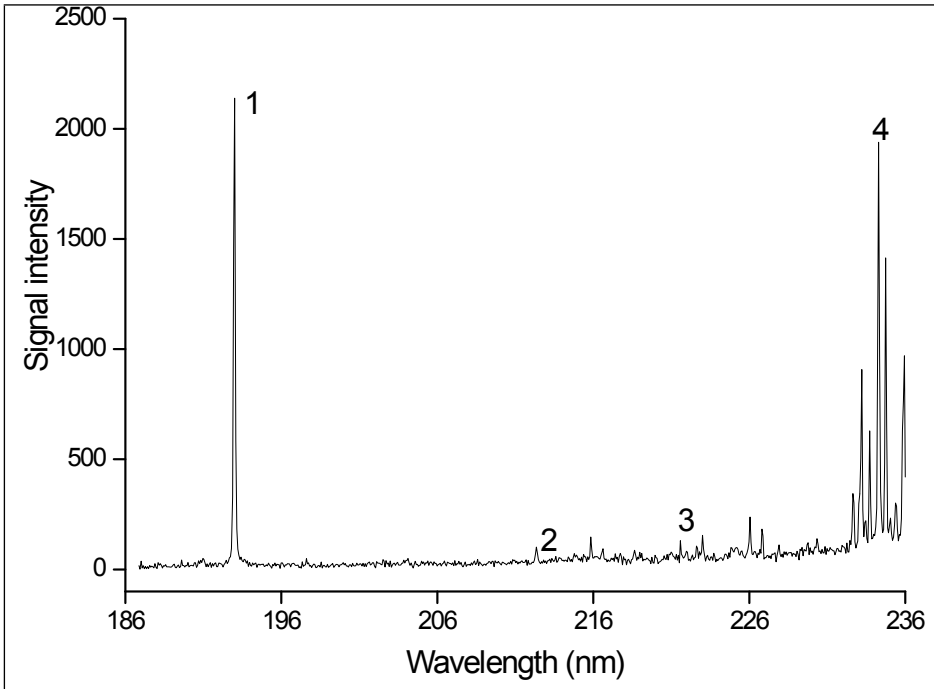


Figure 21S: Emission spectrum from 186 to 236 nm for lipstick sample.

1: C I (193.091)

2: Si I (212.412)

3: Si I (221.667)

4: Fe II (234.349)

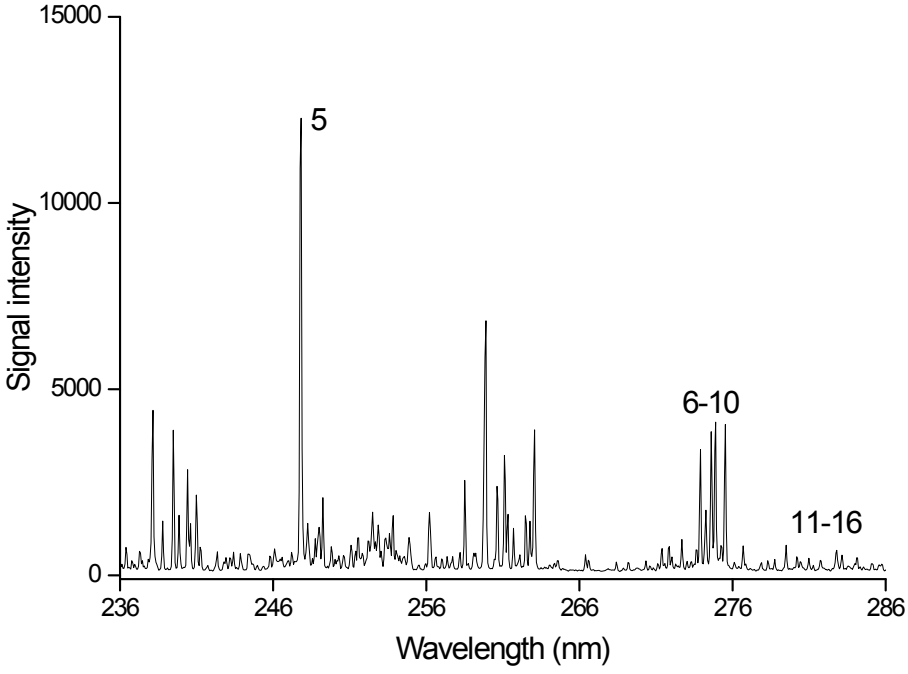


Figure 22S: Emission spectrum from 226 to 286 nm for lipstick sample.

5: C I (247.856)

6: Fe II (274.320)

7: Fe II (274.648)

8: Fe II (274.948)

9: Fe I (275.403)

10: Fe II (275.573)

11: Mg I (277.983)

12: Mg II (279.078)

13: Mg II (279.533)

14: Mg II (279.799)

15: Mg II (280.270)

16: Mg I (285.213)

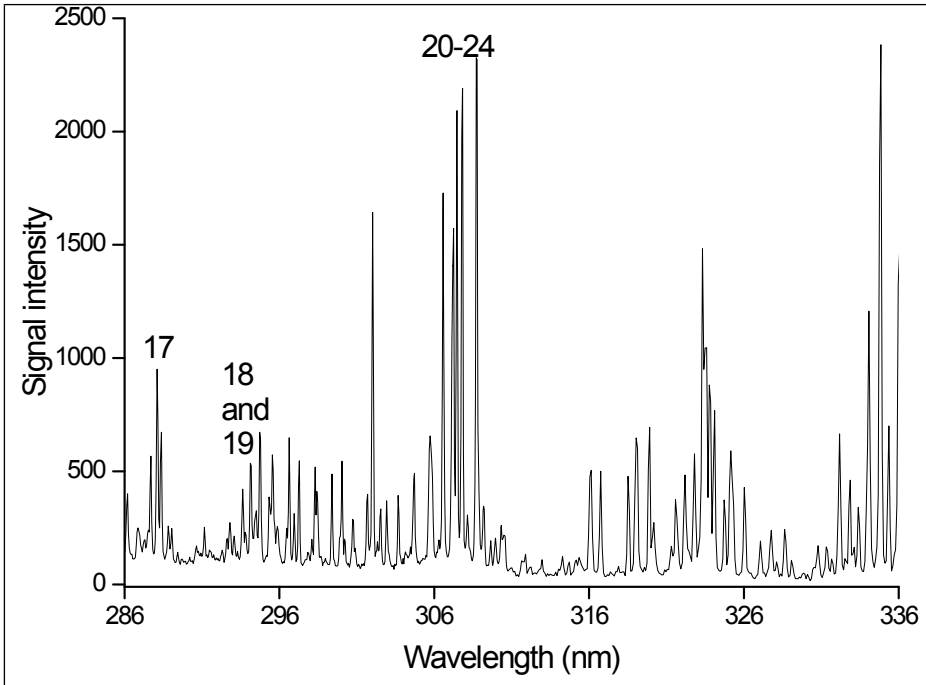


Figure 23S: Emission spectrum from 286 to 336 nm for lipstick sample.

17: Si I (288.157)

18: Mg II (292.863)

19: Mg II (293.651)

20: Ti II (306.622)

21: Ti II (307.297)

22: Ti II (307.522)

23: Ti II (307.864)

24: Ti II (308.802)

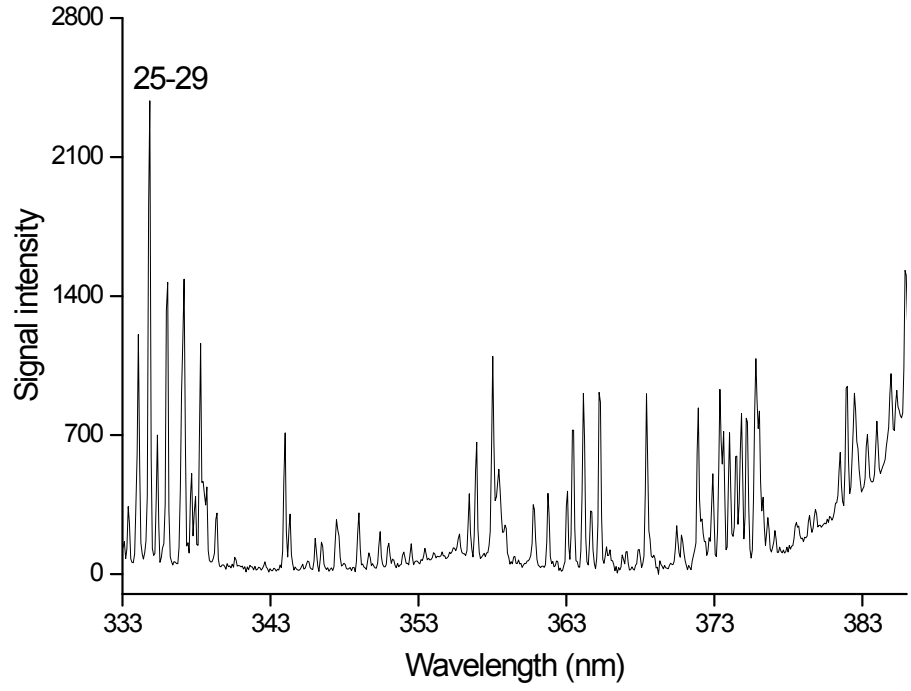


Figure 24S: Emission spectrum from 336 to 386 nm for lipstick sample.

25: Ti I (334.188)

26: Ti II (334.904)

27: Ti II (336.121)

28: Ti II (337.280)

29: Ti II (338.376)

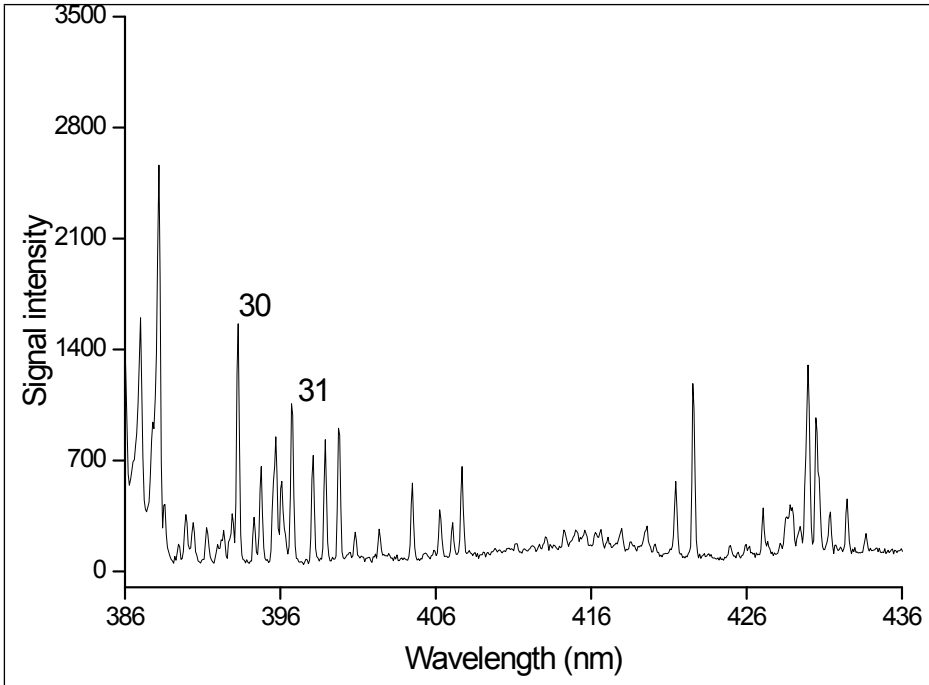


Figure 25S: Emission spectrum from 386 to 436 nm for lipstick sample.

30: Ca II (393.366)

31: Ca II (396.847)

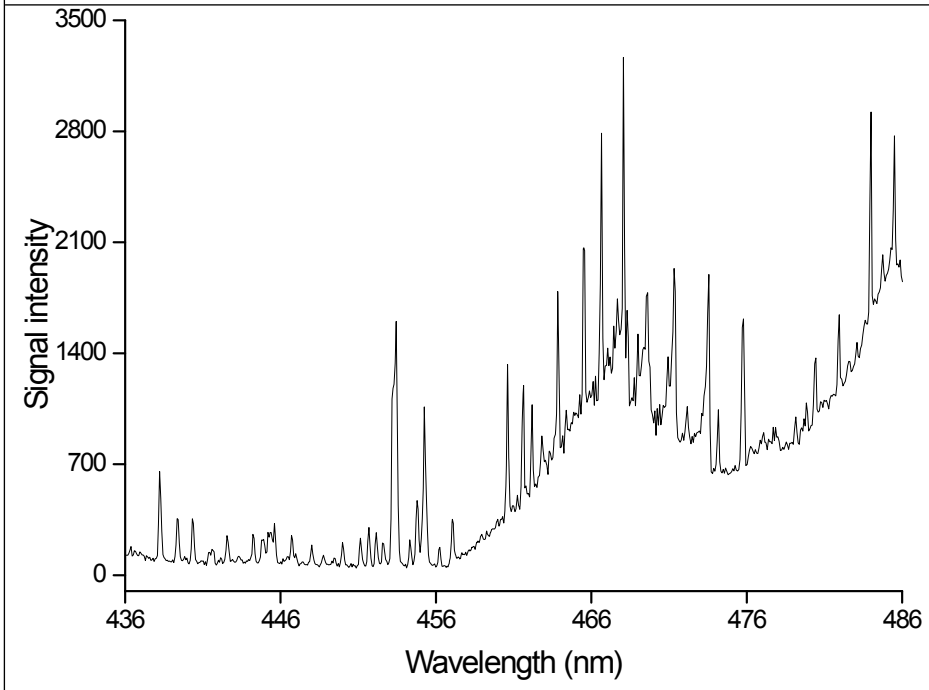


Figure 26S: Emission spectrum from 436 to 486 nm for lipstick sample.

Around 20 emission lines for Ti

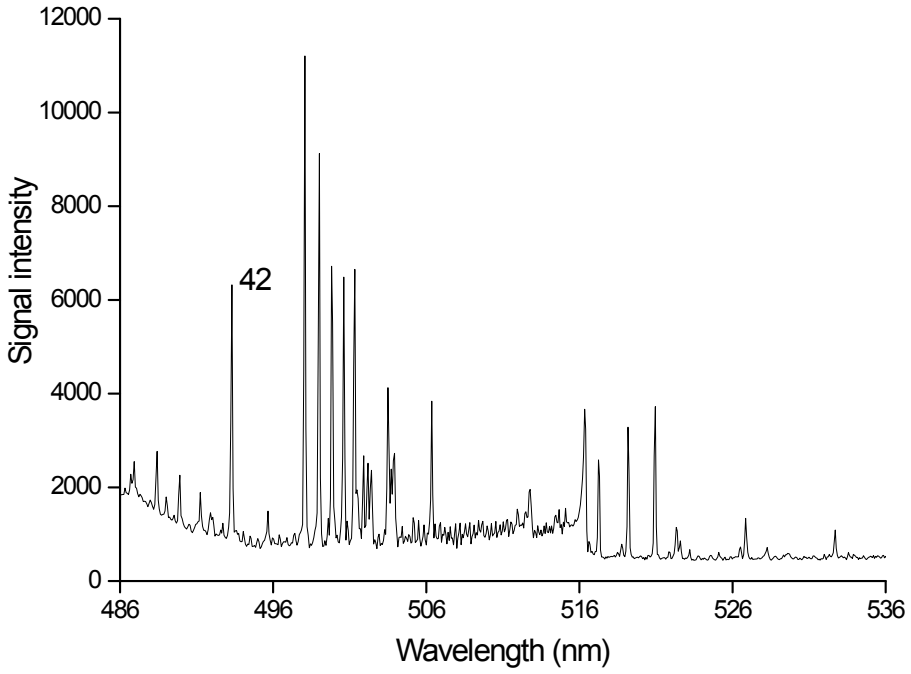


Figure 27S: Emission spectrum from 486 to 536 nm for lipstick sample.

42: Ba II (493.409)

Twenty emission lines for Ti and 4 emission lines for Mg.

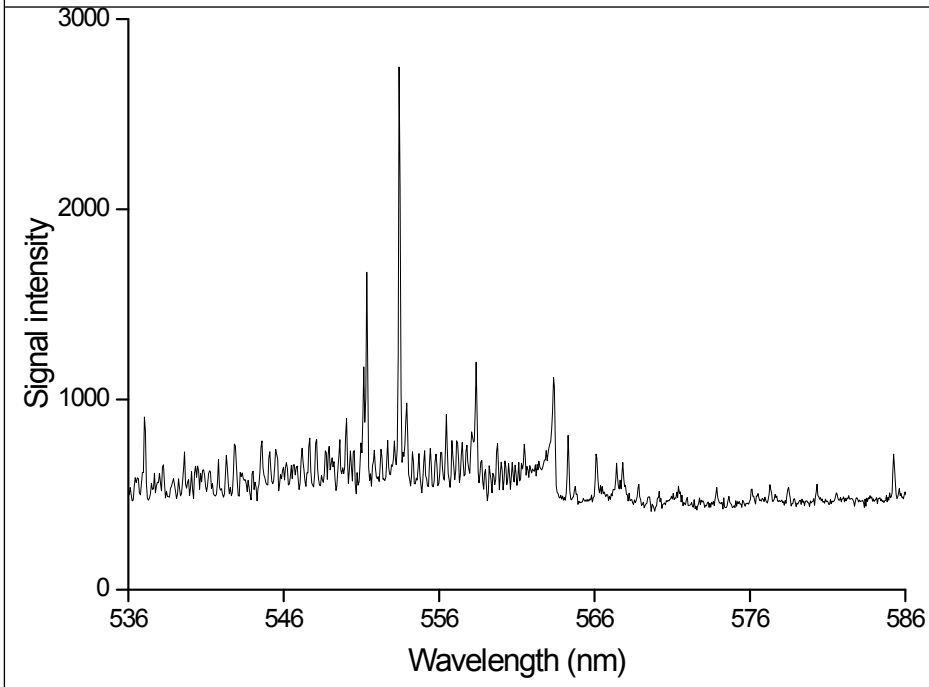


Figure 28S: Emission spectrum from 536 to 586 nm for lipstick sample.

Around 20 emission lines for Ti and Fe

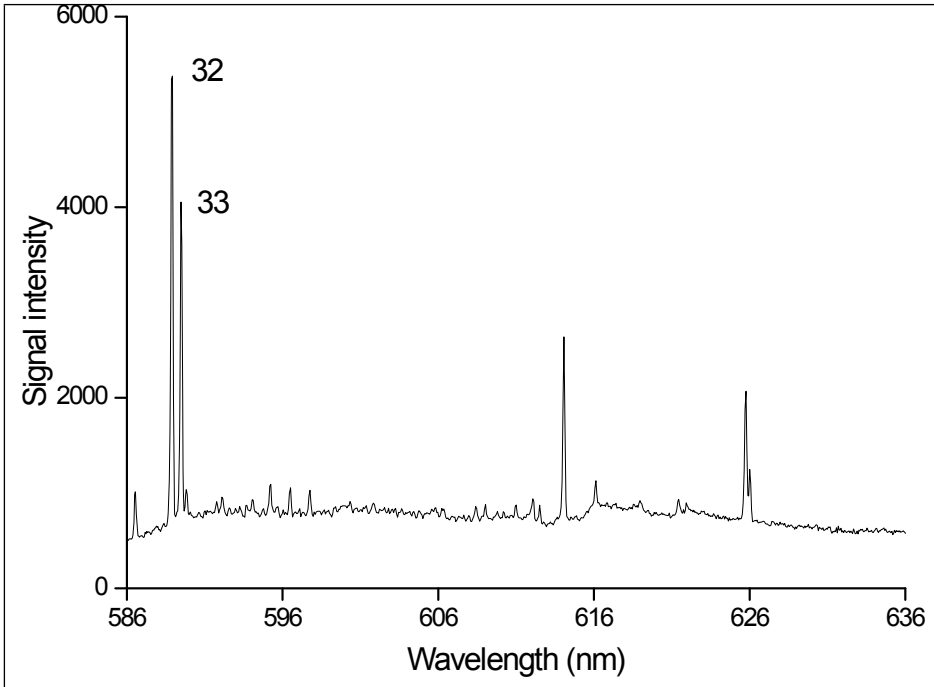


Figure 29S: Emission spectrum from 586 to 636 nm for lipstick sample.

32: Na I (588.995)

33: Na I (589.593)

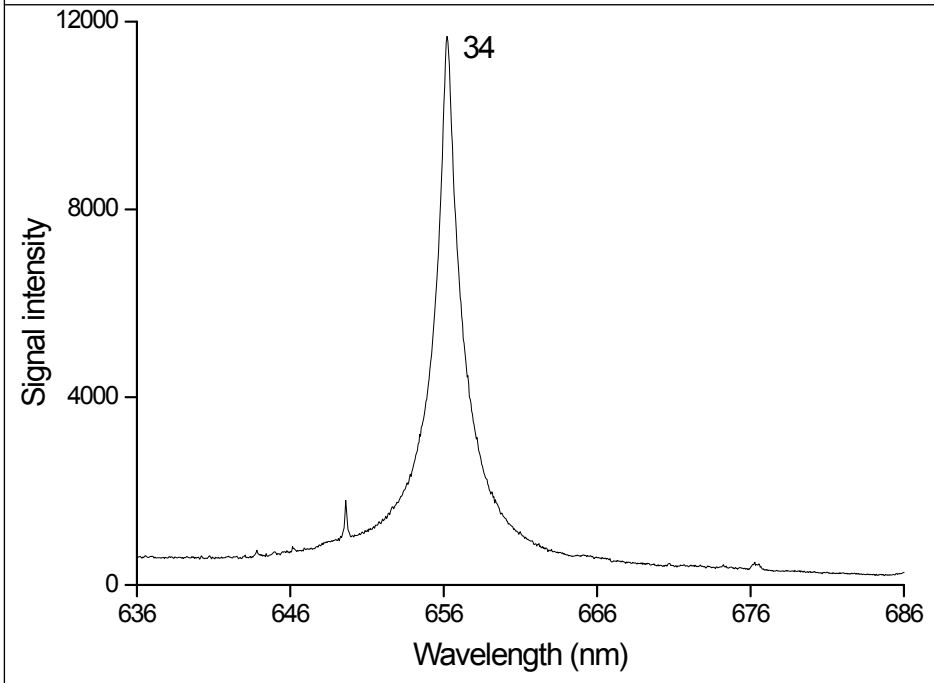


Figure 30S: Emission spectrum from 636 to 686 nm for lipstick sample.

34: H I (656.286)

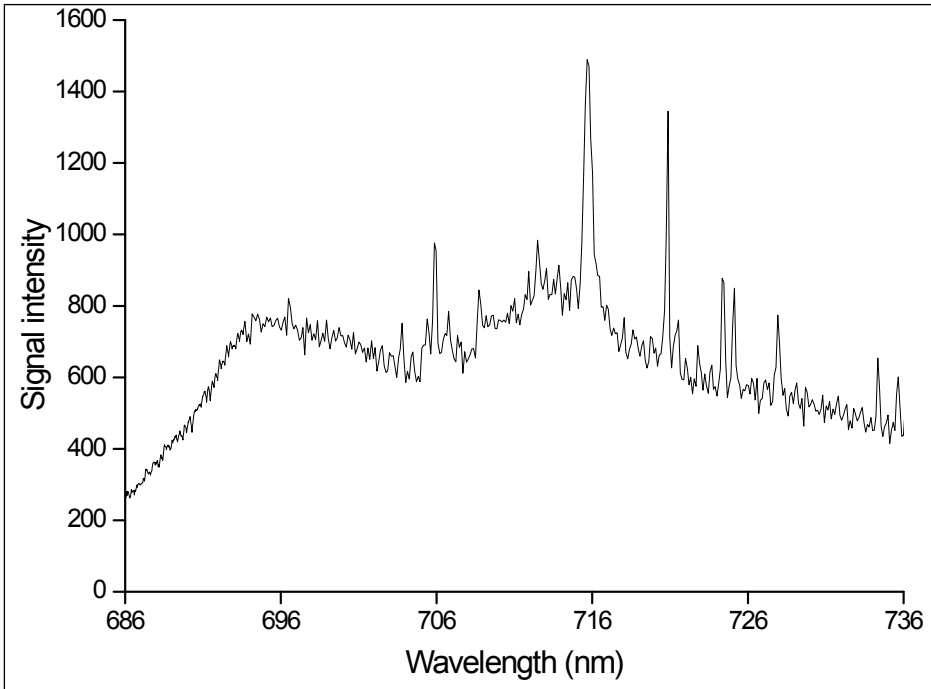


Figure 31S: Emission spectrum from 686 to 736 nm for lipstick sample.

No emission line was identified

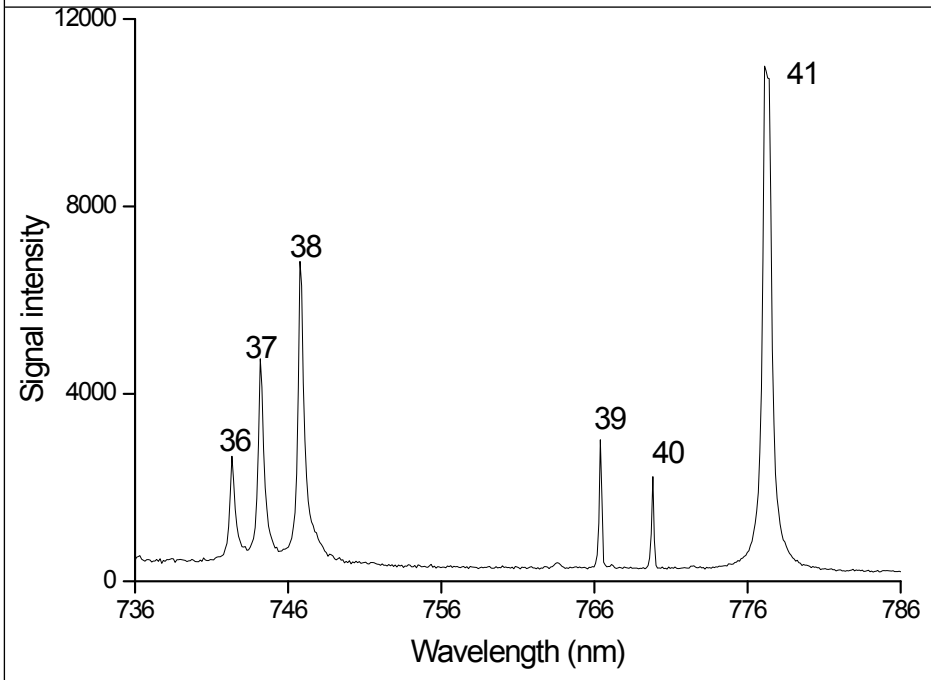


Figure 32S: Emission spectrum from 736 to 786 nm for lipstick sample.

36: N I (742.368)

37: N I (744.230)

38: N I (746.831)

39: K I (766.490)

40: K I (769.896)

41: O I (777.421)

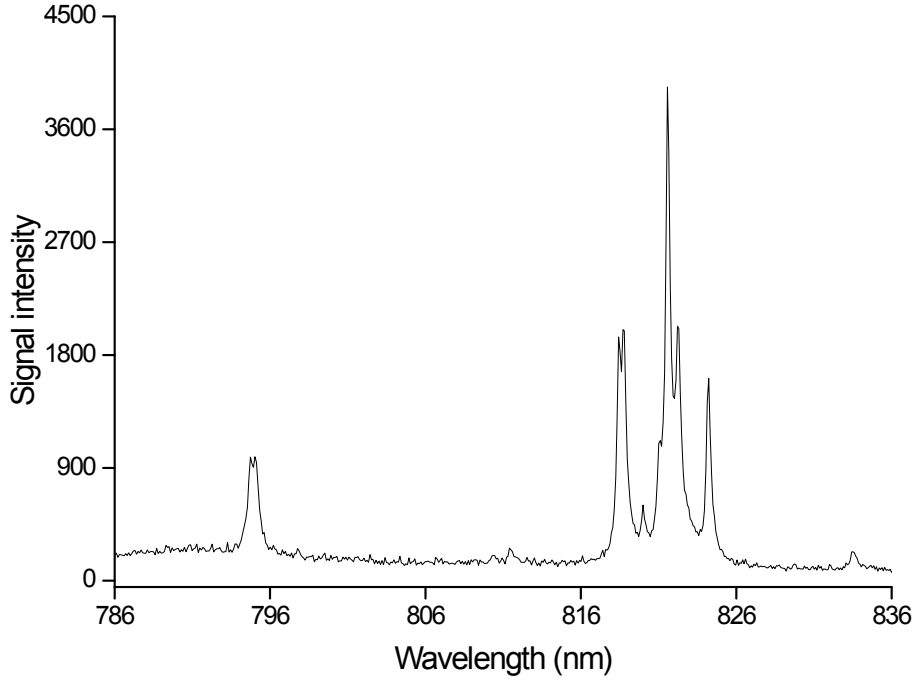


Figure 33S: Emission spectrum from 786 to 836 nm for lipstick sample.

Several O and N (7 lines) emission lines

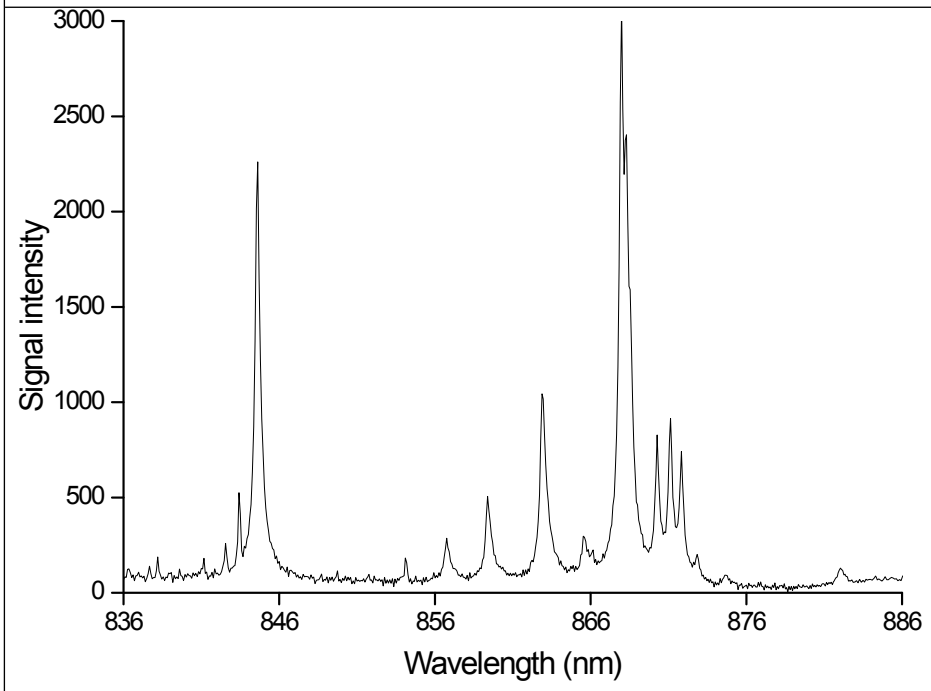


Figure 34S: Emission spectrum from 836 to 886 nm for lipstick sample.

Several O and N (16 lines) emission lines

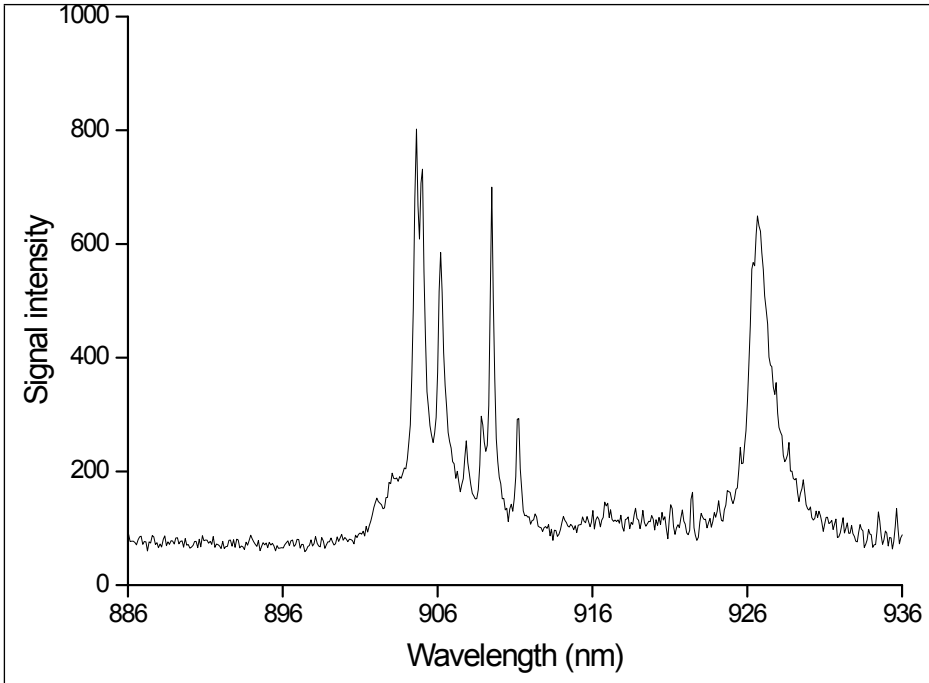


Figure 35S: Emission spectrum from 886 to 936 nm for lipstick sample.

No emission lines were identified

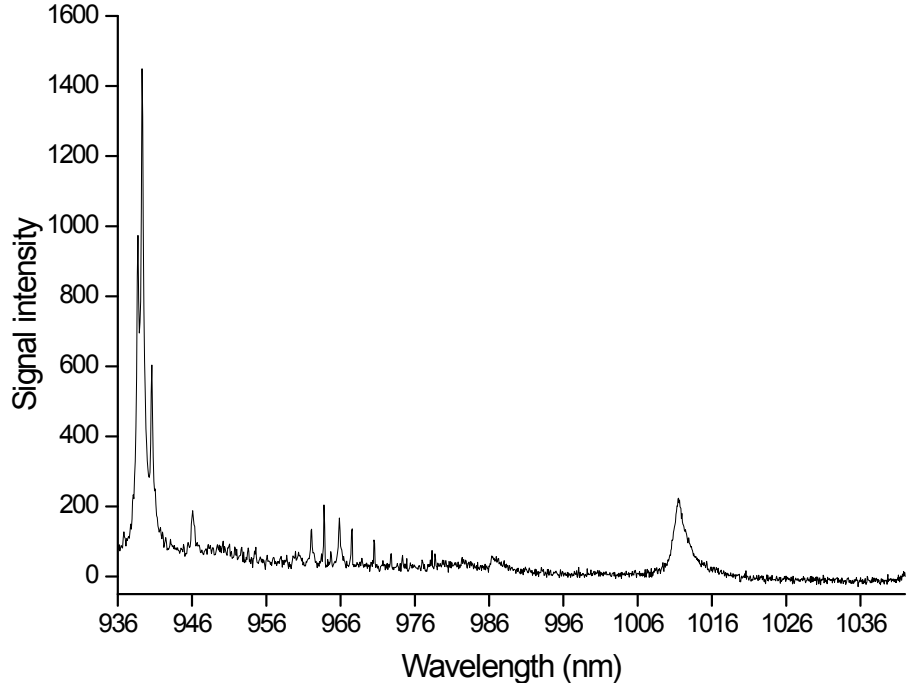


Figure 36S: Emission spectrum from 936 to 1042 nm for lipstick sample.

No emission lines were identified

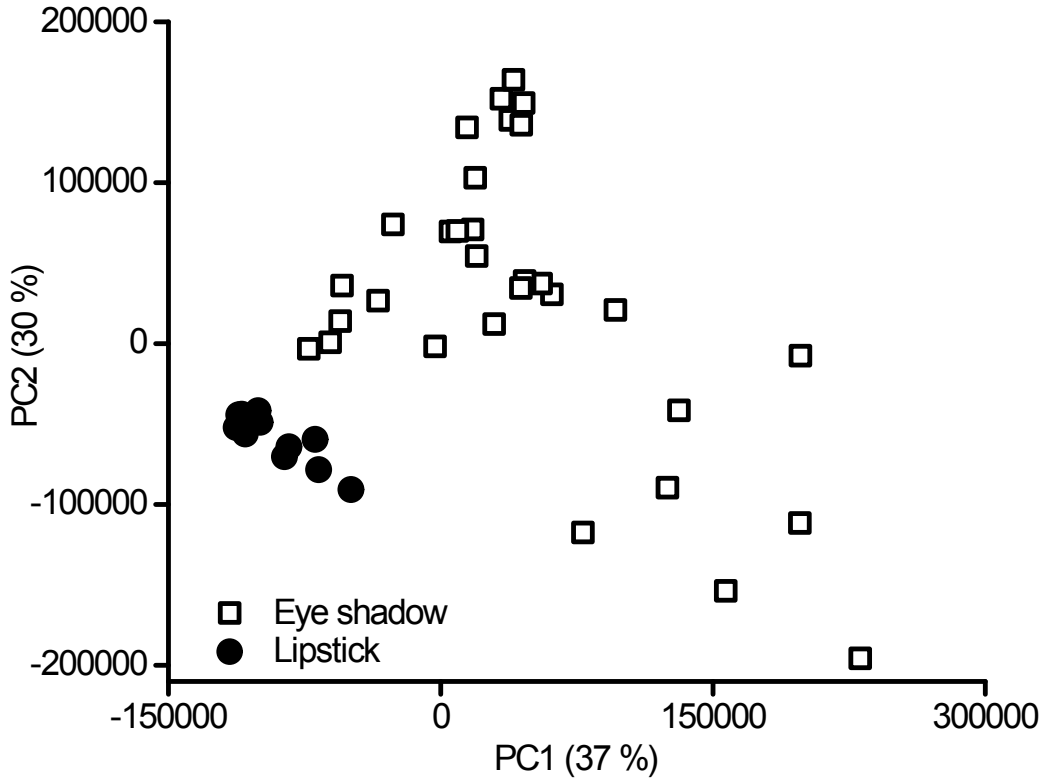
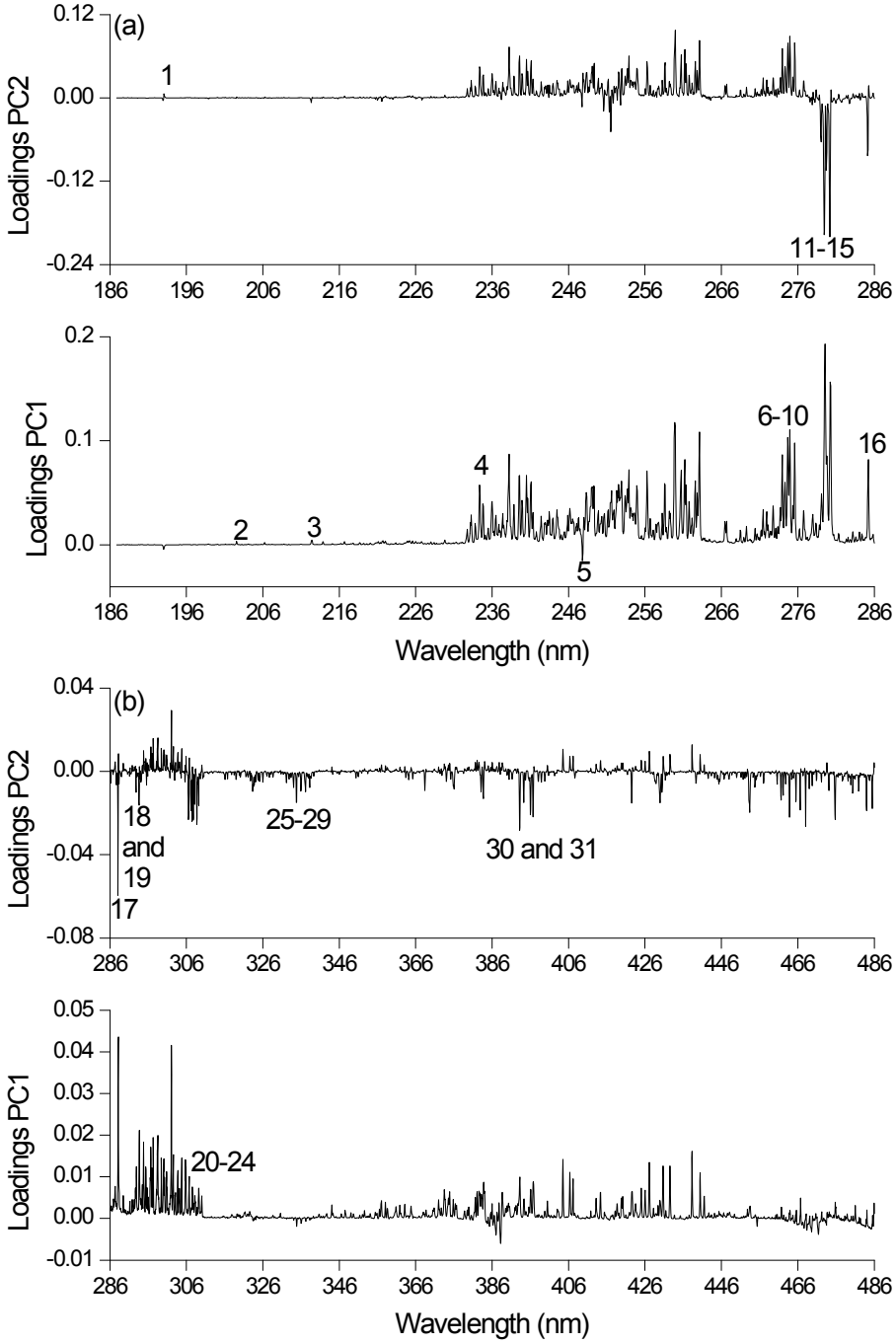


Figure 37S: **Scores plot of the results of eye shadow and lipstick samples by LIBS.**

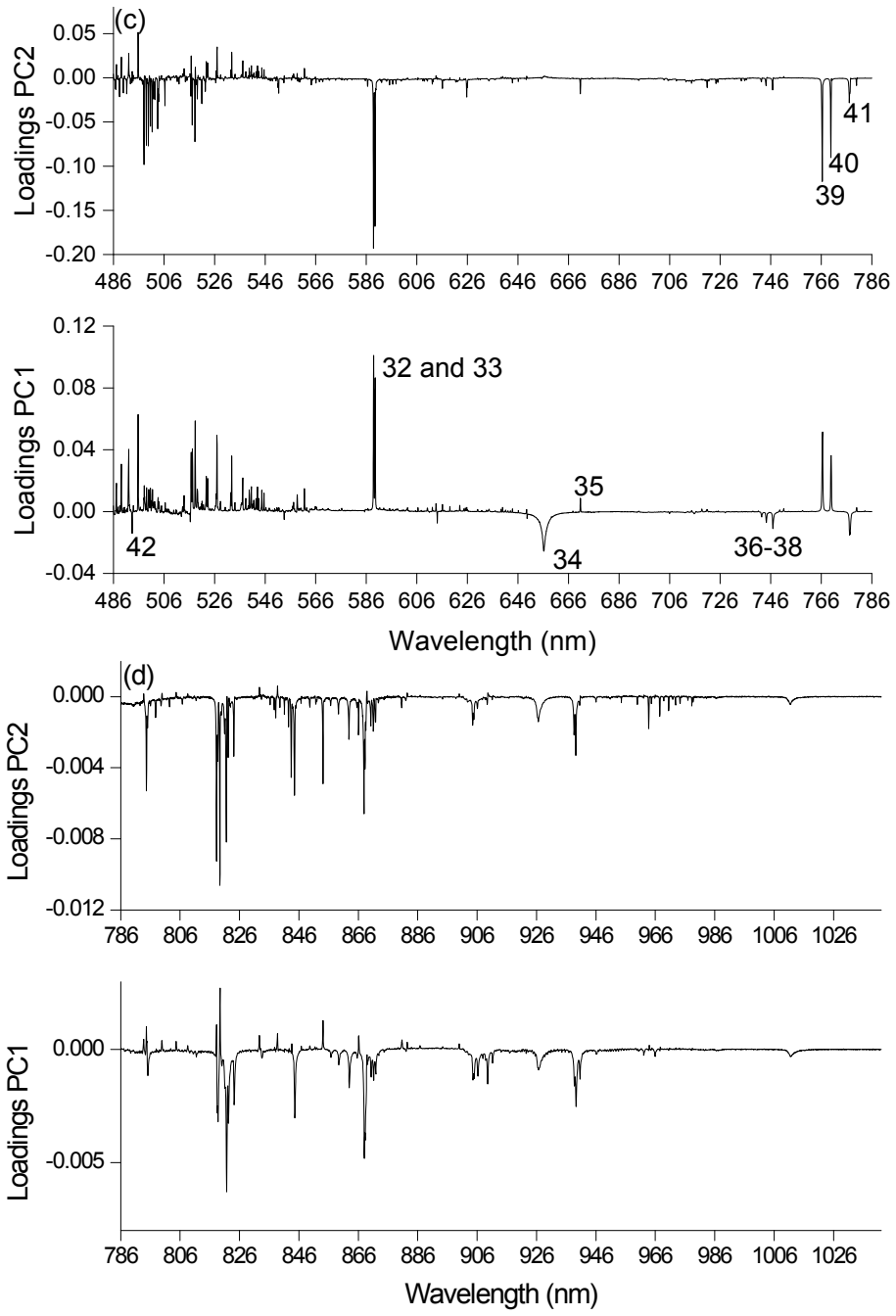
Loadings plots for a PCA calculated with eye shadow and lipstick emission data together.



1: C I (193.091)
2: Si I (212.412)
3: Si I (221.667)
4: Fe II (234.349)
5: C I (247.856)
6: Fe II (274.320)
7: Fe II (274.648)
8: Fe II (274.948)
9: Fe I (275.403)
10: Fe II (275.573)
11: Mg I (277.983)
12: Mg II (279.078)
13: Mg II (279.533)
14: Mg II (279.799)
15: Mg II (280.270)
16: Mg I (285.213)

17: Si I (288.157)
18: Mg II (292.863)
19: Mg II (293.651)
20: Ti II (306.622)
21: Ti II (307.297)
22: Ti II (307.522)
23: Ti II (307.864)
24: Ti II (308.802)
25: Ti I (334.188)
26: Ti II (334.904)
27: Ti II (336.121)
28: Ti II (337.280)
29: Ti II (338.376)
30: Ca II (393.366)
31: Ca II (396.847)

From 436 – 486: Around 20 emission lines for Ti



From 486 – 536: Twenty emission lines for Ti and 4 emission lines for Mg.

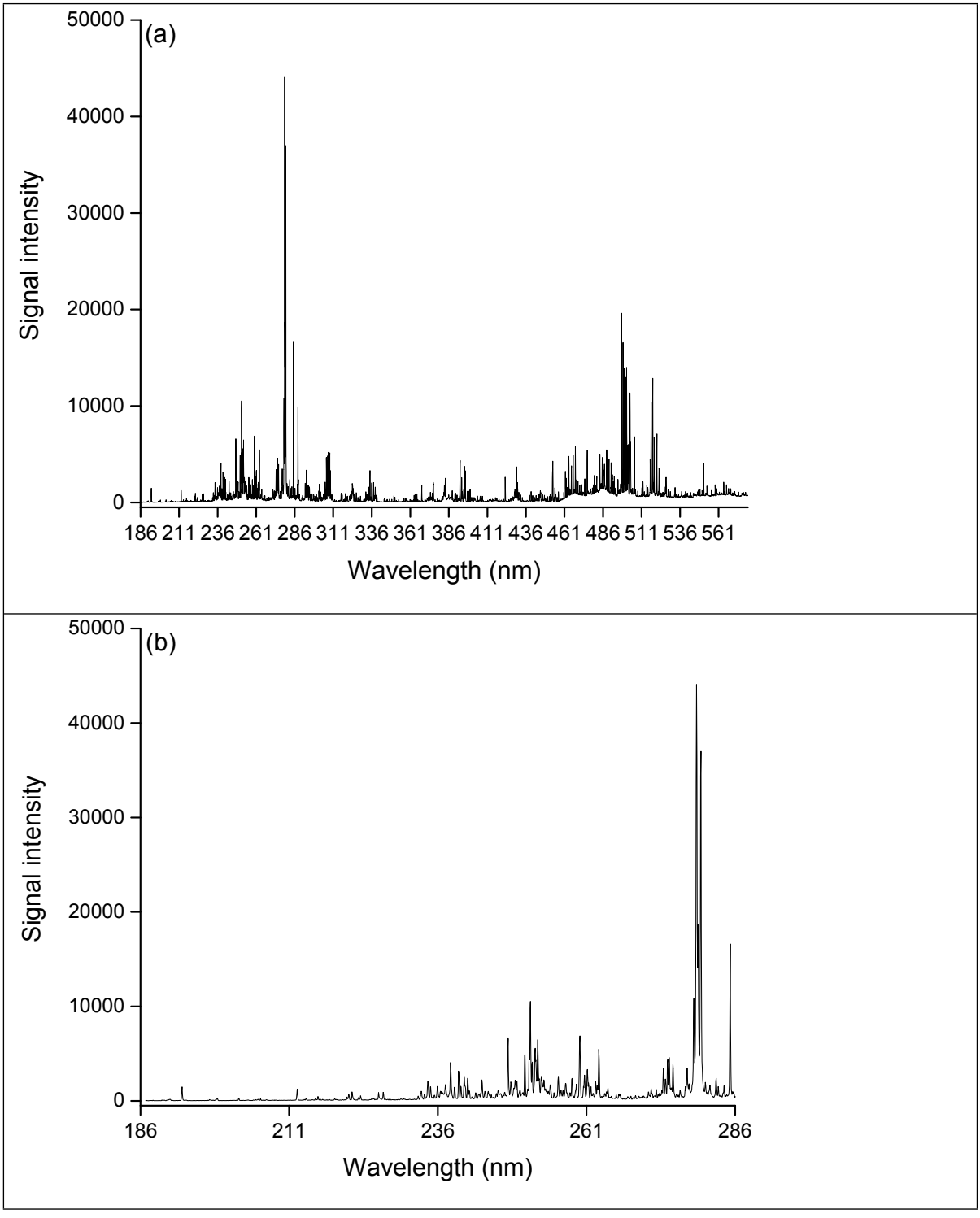
From 536 – 586: Around 20 emission lines for Ti and Fe

32: Na I (588.995)
33: Na I (589.593)
34: H I (656.286)
35: Li I (670.776)
36: N I (742.368)
37: N I (744.230)
38: N I (746.831)
39: K I (766.490)
40: K I (769.896)
41: O I (777.421)
42: Ba II (493.409)

From 786 – 836: Several O and N (7 lines) emission lines

From 836 – 886: Several O and N (16 lines) emission lines

Figure 38S – Loadings plots of PCA calculated for eye shadow and lipstick samples analysed by LIBS. For better visualization, the spectral range was divided in 4 different figures (a – d).


(a)
Signal intensity
50000
40000
30000
20000
10000
0
186 211 236 261 286 311 336 361 386 411 436 461 486 511 536 561
Wavelength (nm)
(b)
Signal intensity
50000
40000
30000
20000
10000
0
186
211
236
261
286
Wavelength (nm)

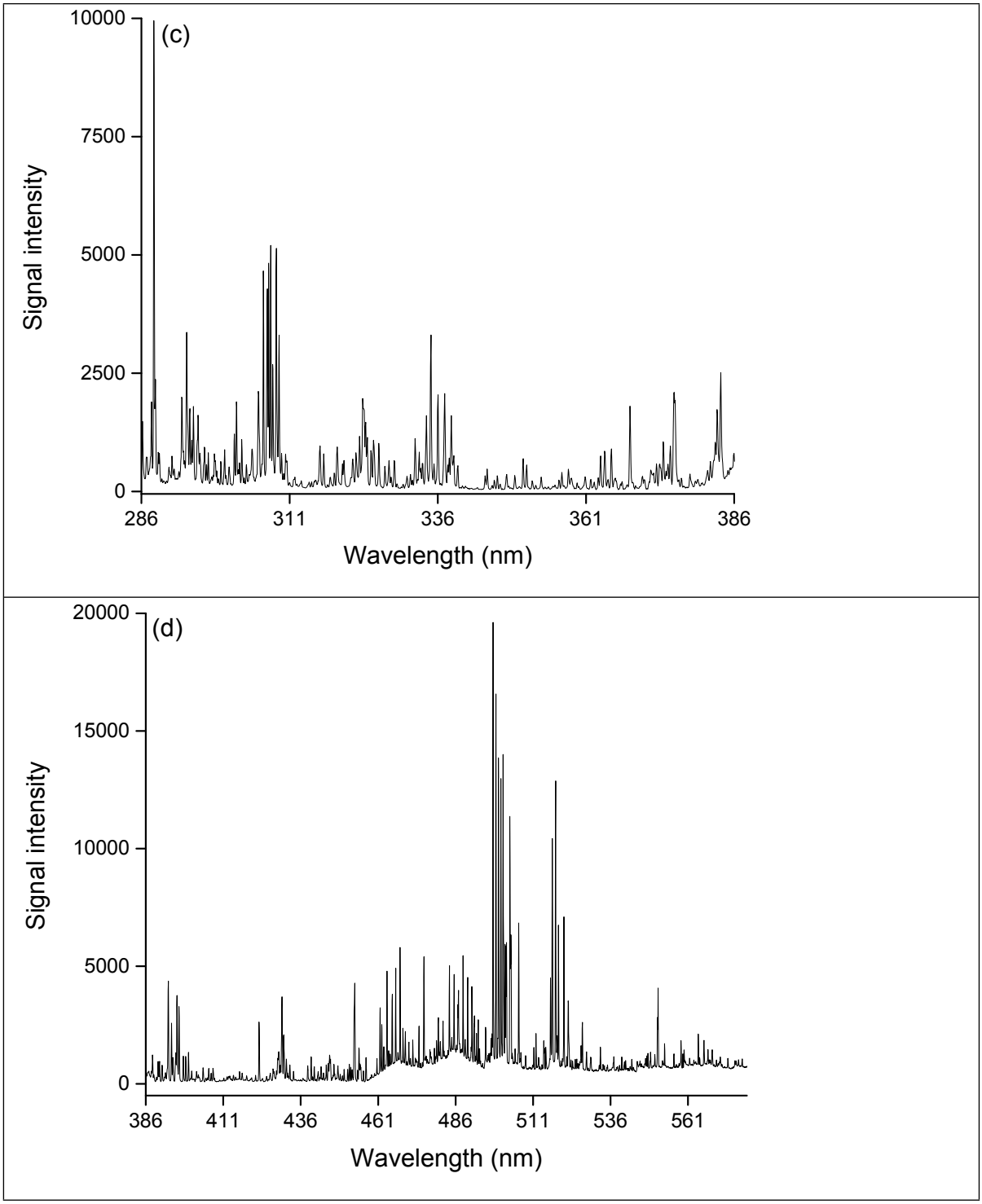
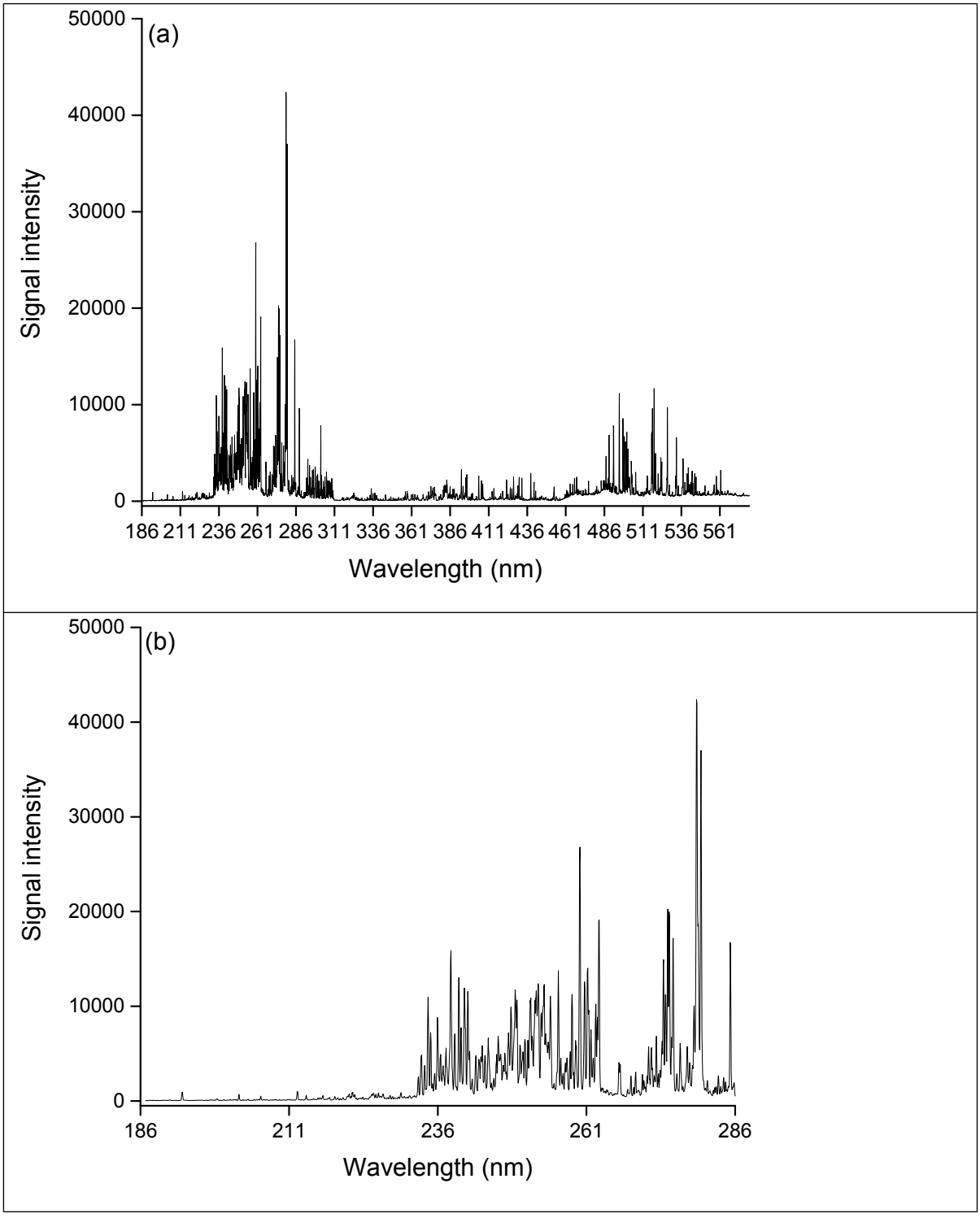


Figure 39S – Average emission spectra for eye shadow samples with elements concentration below 5 mg kg^{-1} (a: spectral range from 186 – 580, b: spectral range from 186 – 286, c: spectral range from 286 – 386, d: spectral range from 386 – 580 nm).


(a)
Signal intensity
50000
40000
30000
20000
10000
0
186 211 236 261 286 311 336 361 386 411 436 461 486 511 536 561
Wavelength (nm)
(b)
Signal intensity
50000
40000
30000
20000
10000
0
186
211
236
261
286
Wavelength (nm)

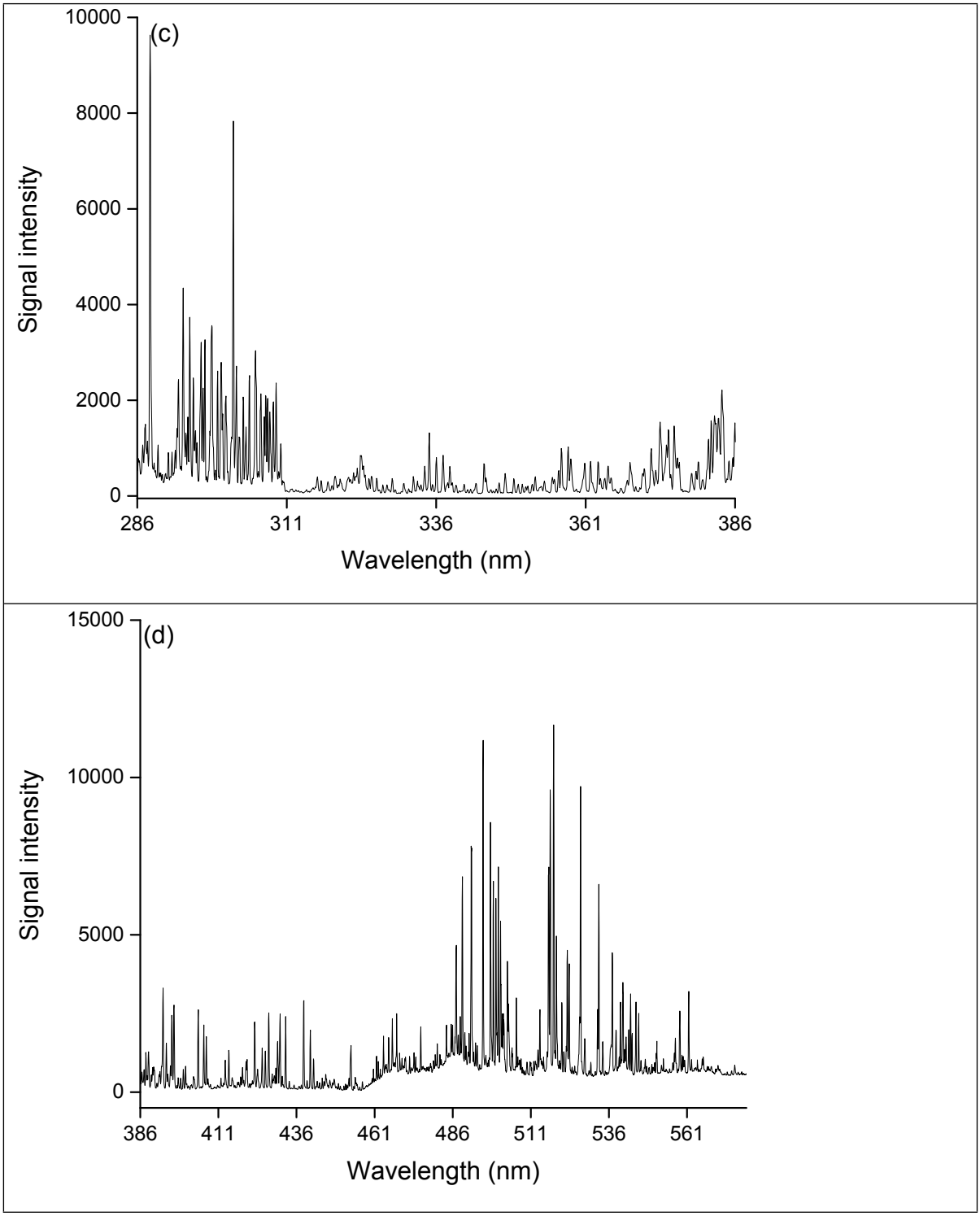
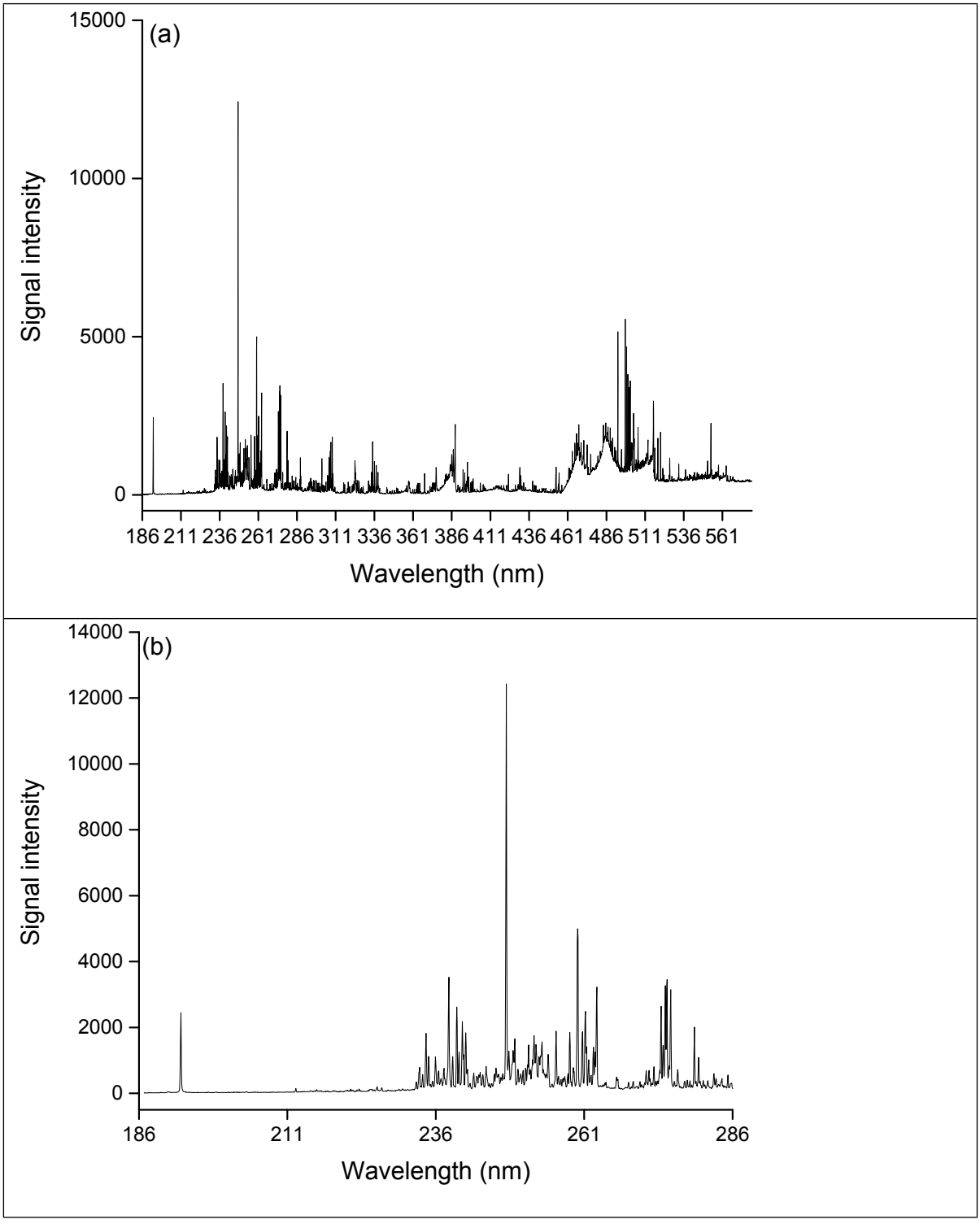


Figure 40S – Average emission spectra for eye shadow samples with elements concentration above 5 mg kg^{-1} (a: spectral range from 186 – 580, b: spectral range from 186 – 286, c: spectral range from 286 – 386, d: spectral range from 386 – 580 nm).


(a)
15000
10000
5000
0
Signal intensity
186 211 236 261 286 311 336 361 386 411 436 461 486 511 536 561
Wavelength (nm)
(b)
14000
12000
10000
8000
6000
4000
2000
0
Signal intensity
186
211
236
261
286
Wavelength (nm)

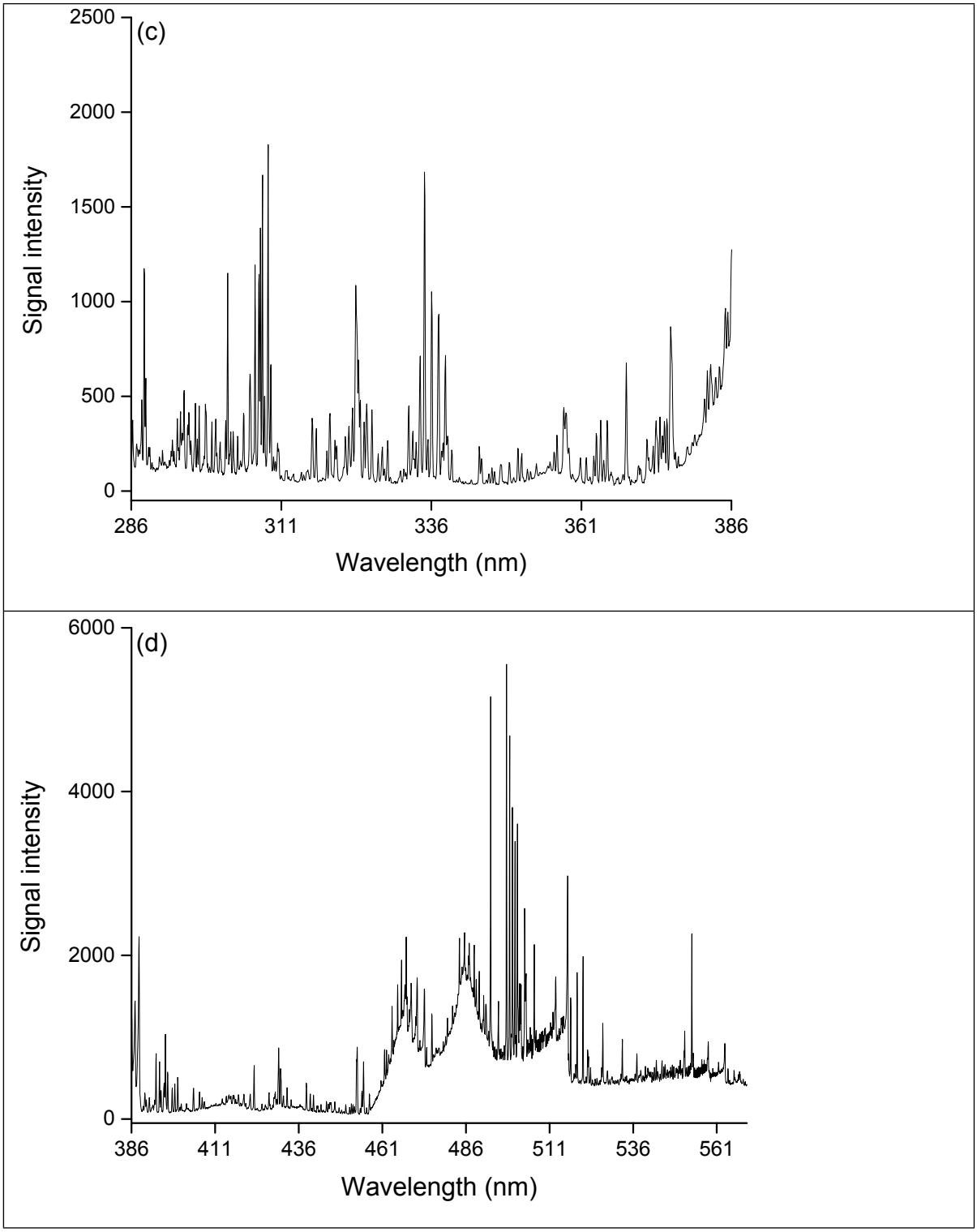
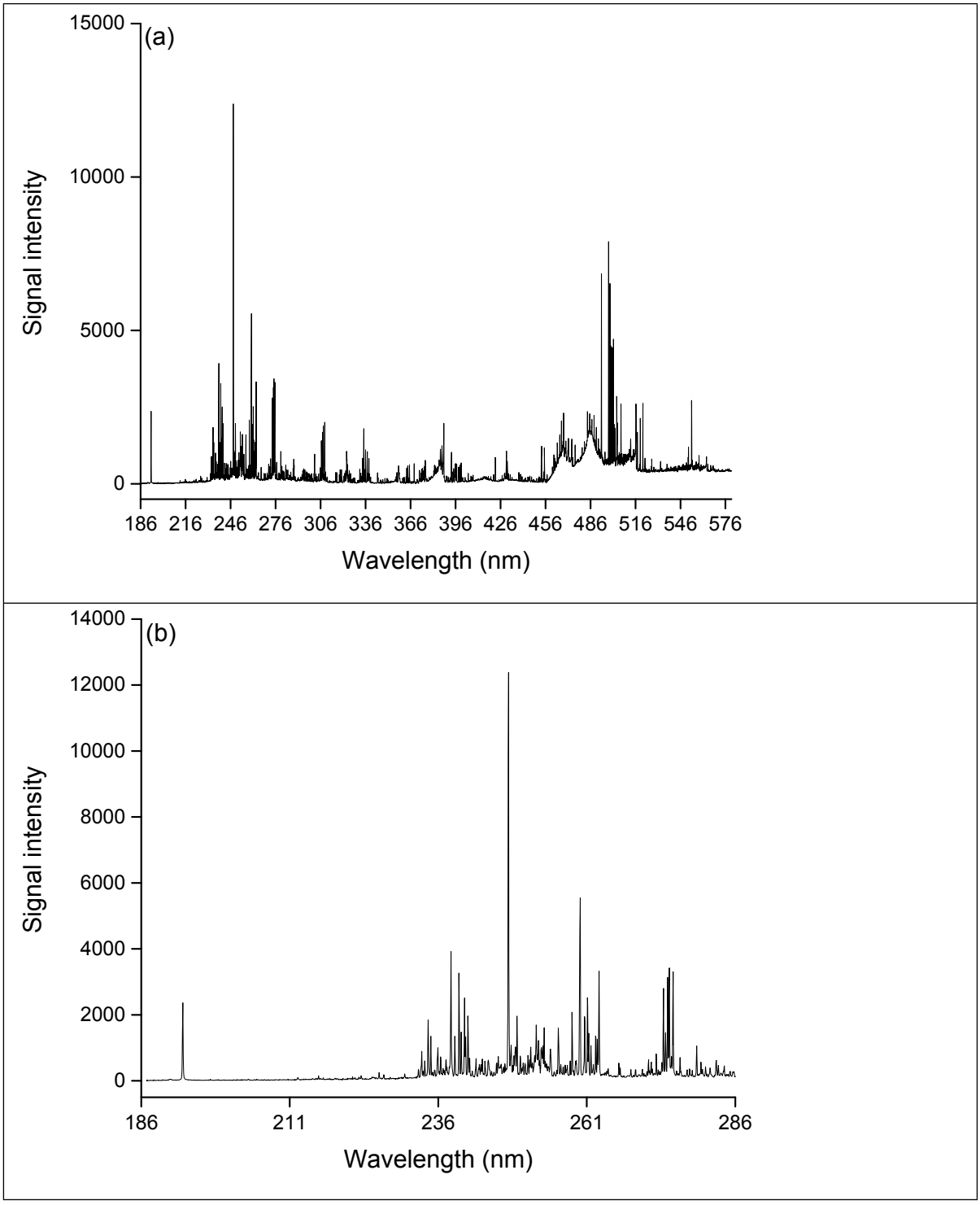


Figure 41S – Average emission spectra for lipstick samples with elements concentration below 5 mg kg^{-1} (a: spectral range from 186 – 580, b: spectral range from 186 – 286, c: spectral range from 286 – 386, d: spectral range from 386 – 580 nm).


(a)
Signal intensity
15000
10000
5000
0
186 216 246 276 306 336 366 396 426 456 486 516 546 576
Wavelength (nm)
(b)
Signal intensity
14000
12000
10000
8000
6000
4000
2000
0
186 211 236 261 286
Wavelength (nm)

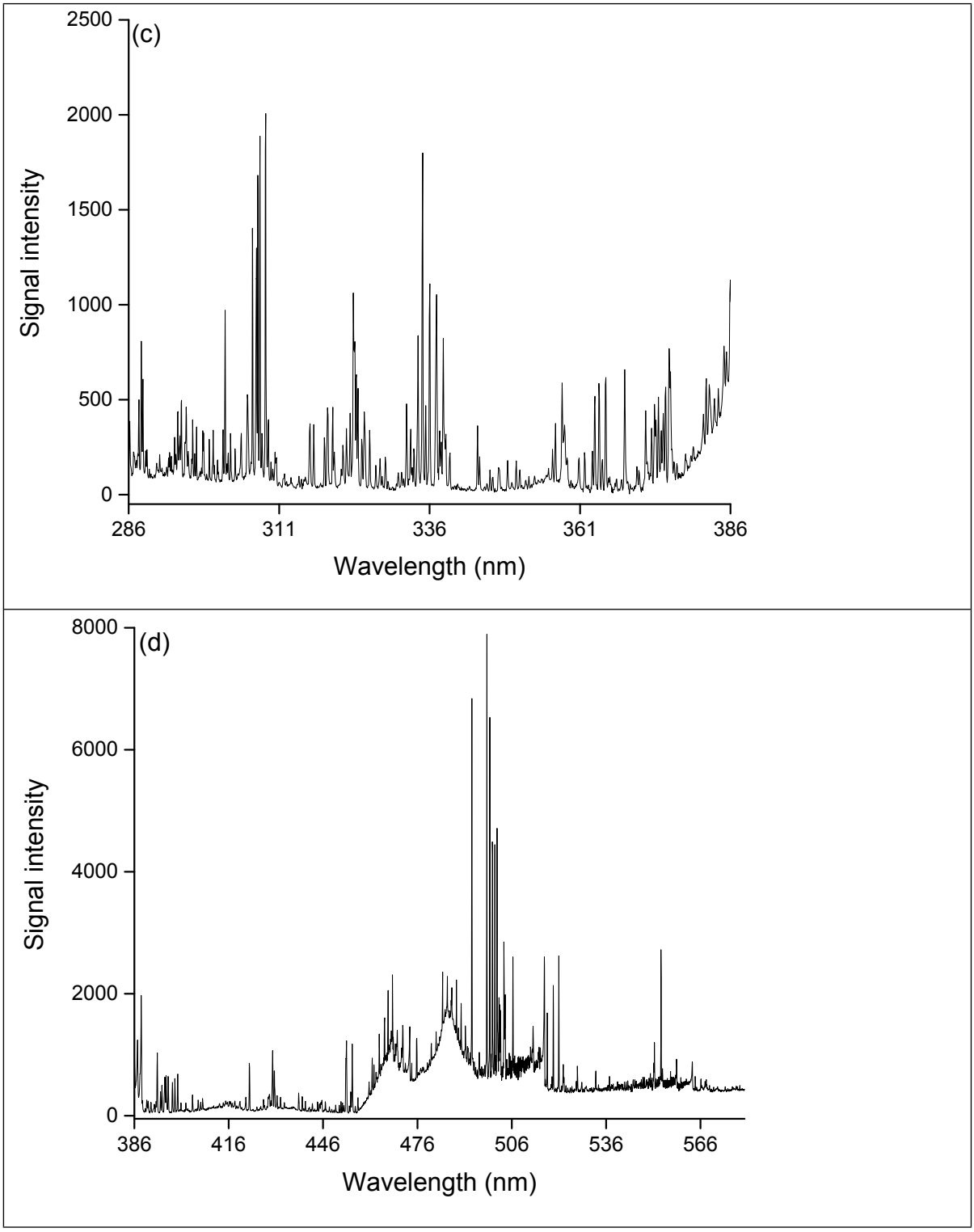


Figure 42S – Average emission spectra for lipstick samples with elements concentration above 5 mg kg^{-1} (a: spectral range from 186 – 580, b: spectral range from 186 – 286, c: spectral range from 286 – 386, d: spectral range from 386 – 580 nm).