

Supporting information

Forensic analysis of hand-written documents using laser-induced breakdown spectroscopy (LIBS) and chemometrics

Felipe Ferri Hilario, Matheus Lima de Mello, Edenir Rodrigues Pereira-Filho*

Group of Applied Instrumental Analysis, Department of Chemistry, Federal University of São Carlos, São Carlos, São Paulo State, 13565-905, Brazil

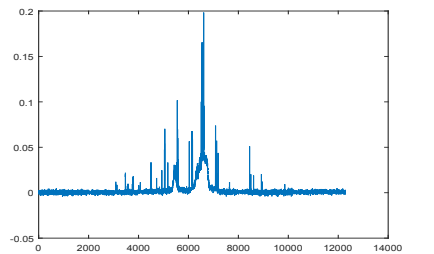
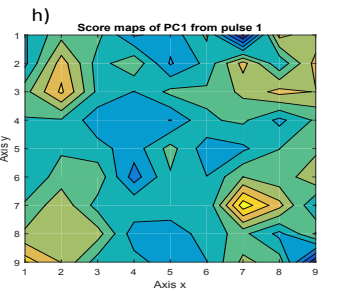
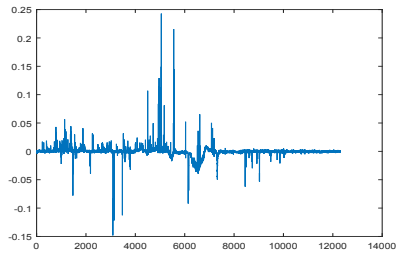
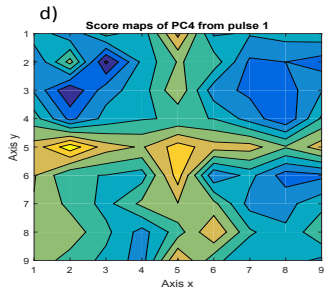
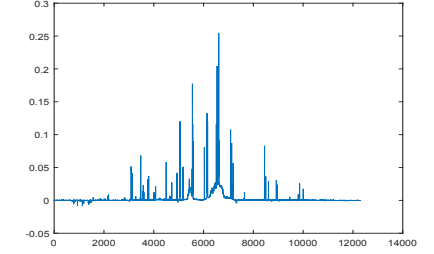
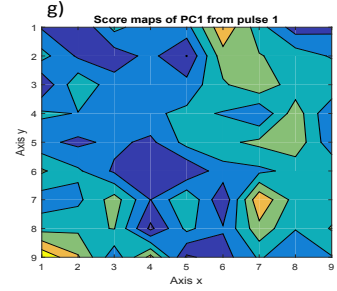
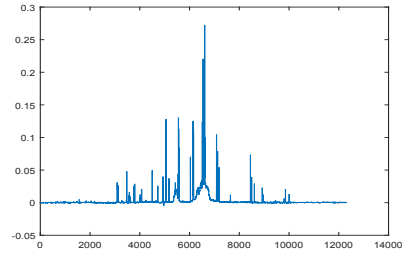
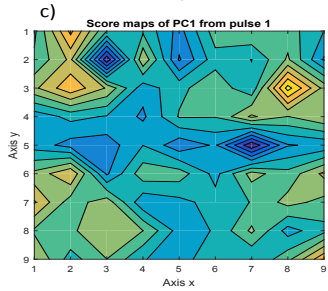
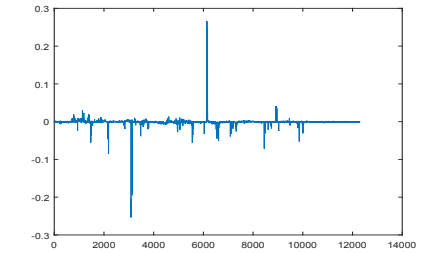
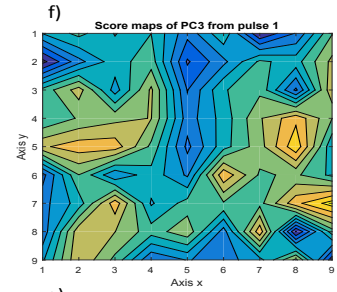
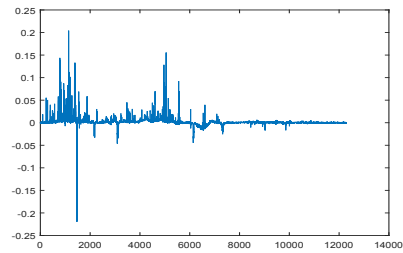
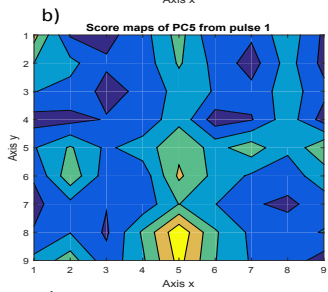
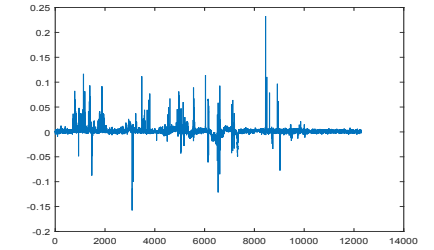
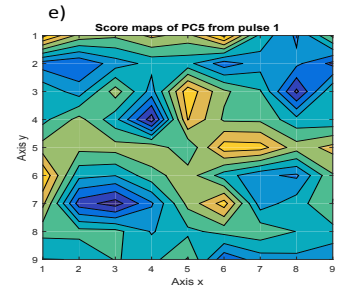
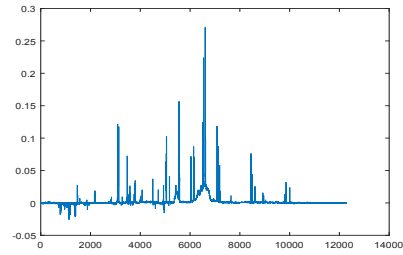
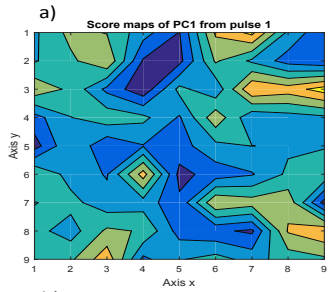
*Corresponding author: erpf@ufscar.br

Table S1. Results obtained from design s2.

Experimental run	Average Score Values			Difference between the average score values			Normalized difference			Dg
	Paper	Black Pen	Blue Pen	Blue-black	Blue-paper	Black-paper	Blue-black (d1)	Blue-paper (d2)	Black-paper (d3)	
1	-2982	8239	5060	3179	8042	1121	0.55	1.00	1.00	0.82
2	-941	4556	-489	5045	451	5496	0.94	0.00	0.43	0.00
3	-667	2821	-193	3014	474	3488	0.52	0.00	0.23	0.07
4	-2586	6133	4456	1677	7042	8719	0.24	0.87	0.75	0.54
5	894	-5410	-1932	3480	2826	6306	0.61	0.31	0.51	0.46
6	-1412	4116	3602	514	5014	5528	0.00	0.60	0.43	0.00
7	-712	-1886	1241	3127	1953	1174	0.54	0.20	0.00	0.00
8	-742	2217	2865	648	3607	2959	0.03	0.42	0.18	0.13
9	1637	-9112	-3759	5352	5396	10748	1.00	0.65	0.95	0.85
10	1842	-8639	-4456	4183	6297	10481	0.76	0.77	0.93	0.81
11	-2135	6850	2830	4020	4966	8985	0.72	0.59	0.78	0.69
12	-1222	4838	3495	1342	4718	5525	0.17	0.56	0.49	0.36
13	2606	-2709	-4774	2065	7380	5315	0.32	0.91	0.41	0.49
14	-1503	3855	5465	1611	6968	6950	0.23	0.86	0.42	0.43
15	47	5249	3790	1459	3744	5492	0.20	0.43	0.40	0.32
16	2779	-5352	-3201	2151	5981	8473	0.34	0.73	0.69	0.55
17	1107	-6159	-1292	4868	2399	6814	0.90	0.26	0.61	0.52

Table S2. Analysis of variance obtained for the regression model of Design 2.

Variation Source	Square Some	Degrees of freedom	Square Media	F test	Tabled F value
Regression	1.157	5	0.231	11.55	3.20
Residue	0.220	11	0.020		
Total	1.377	16	0.086		
Pure Error	0.014	2	0.007		
Lack of Fit	0.207	9	0.023	3.35	19.38
R ²	0.84	R	0.9165		
R ² max	0.990	Rmax	0.995		



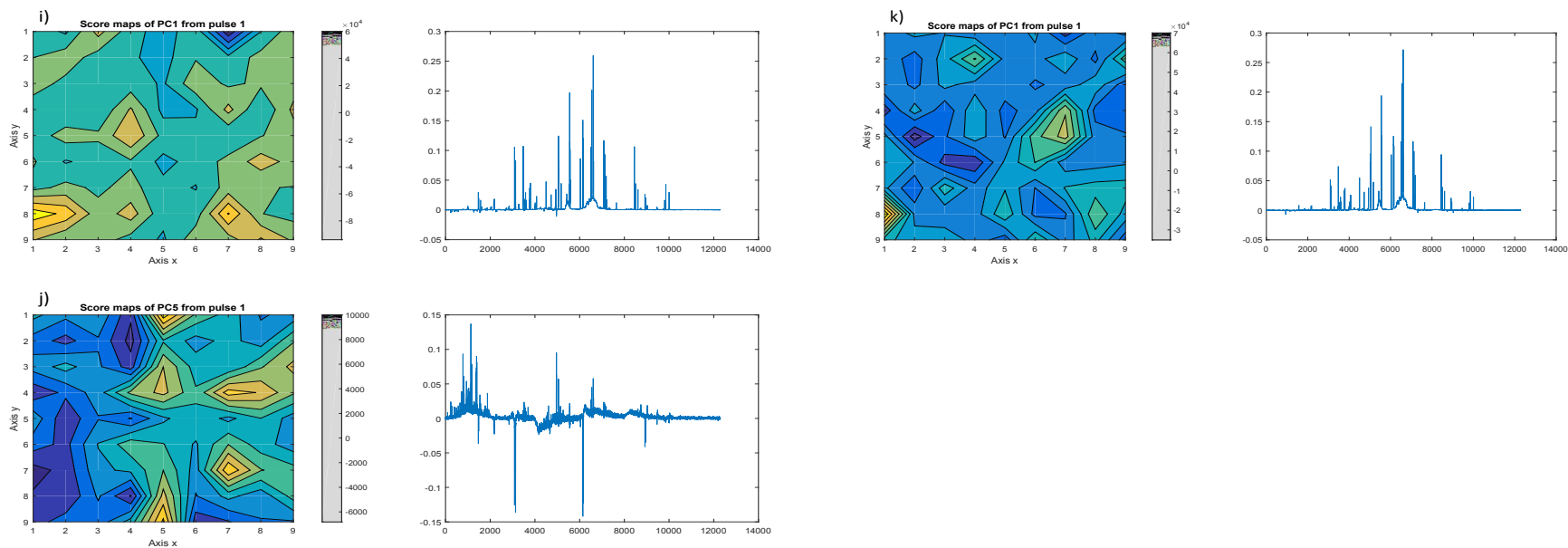
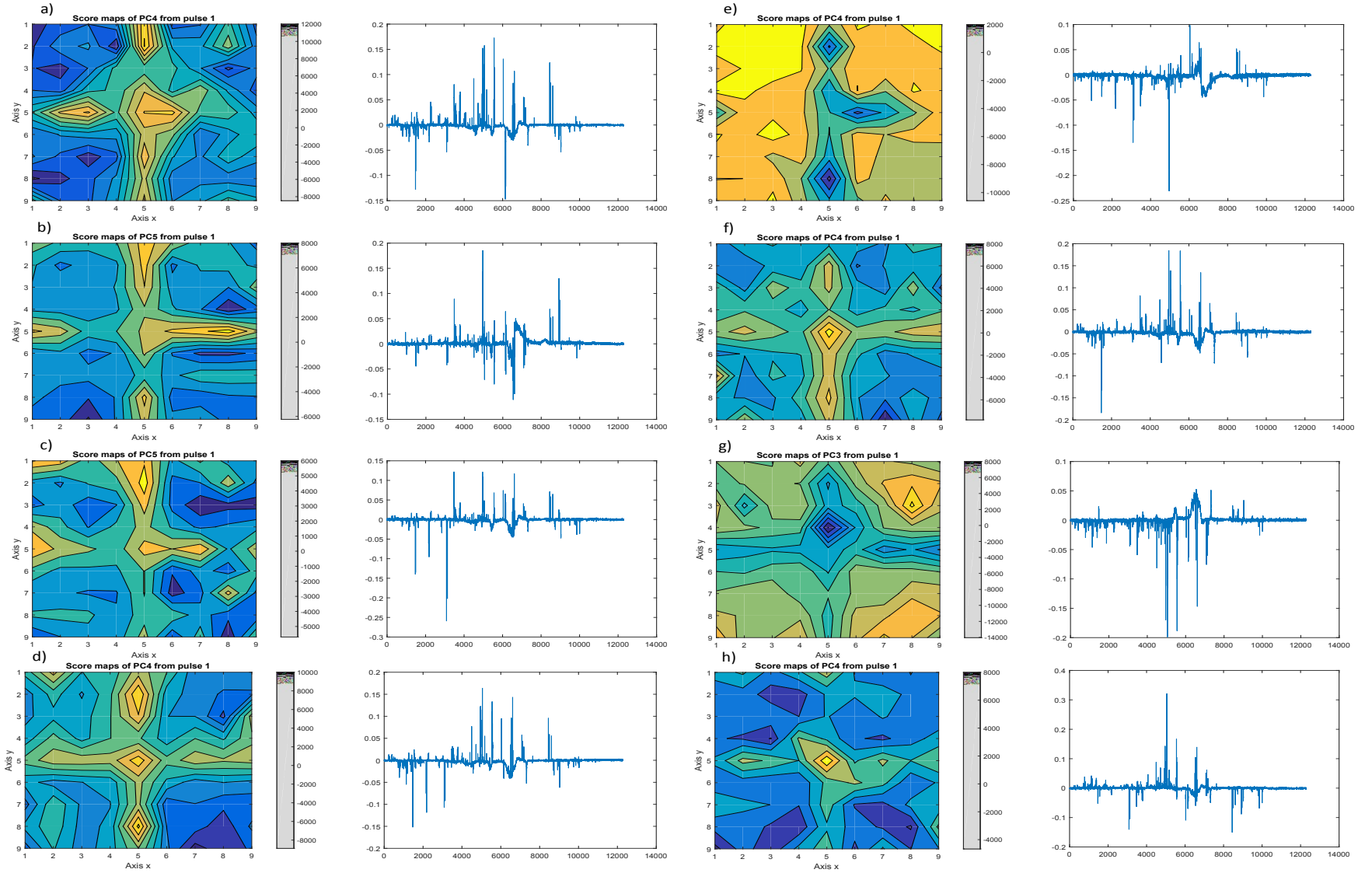
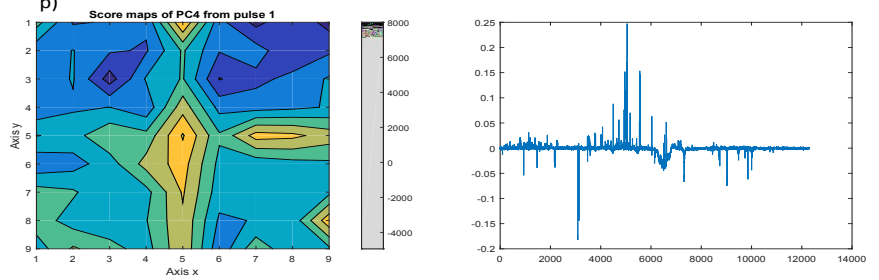
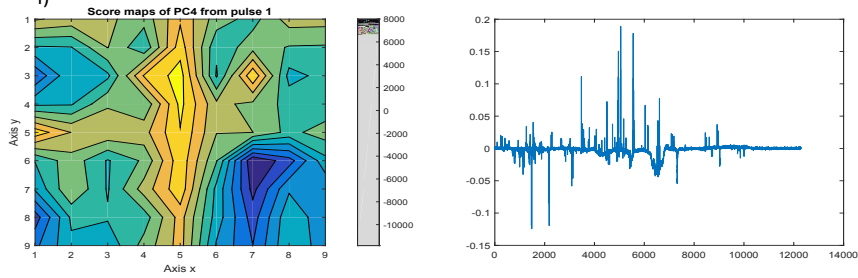
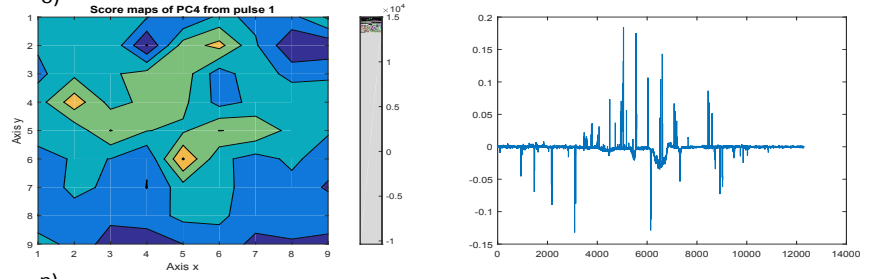
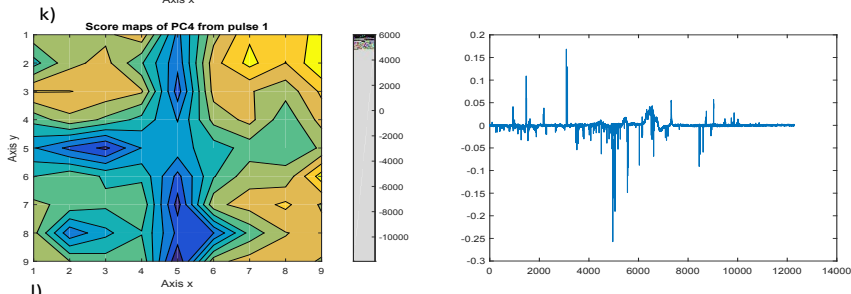
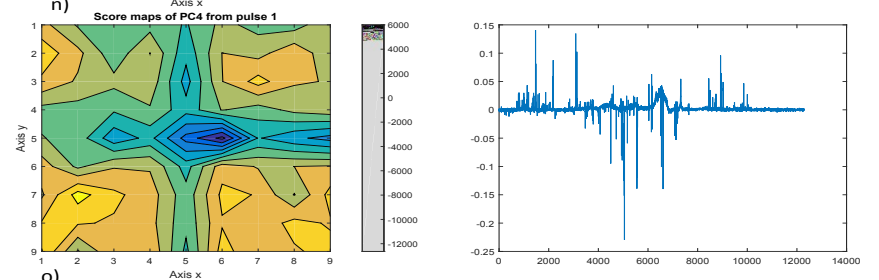
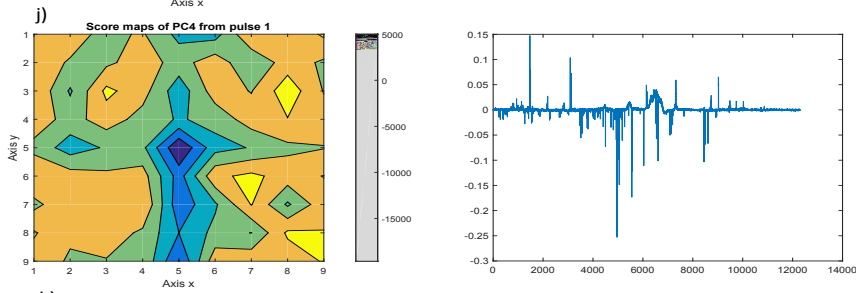
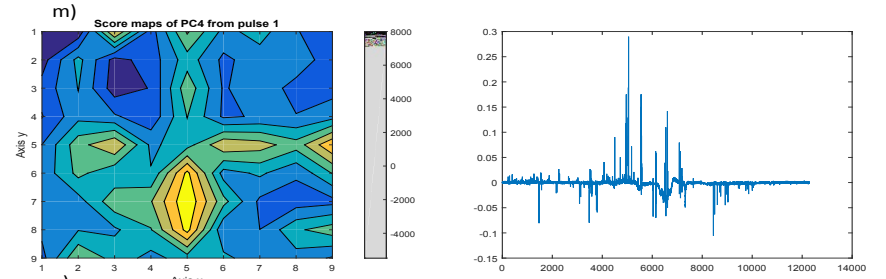
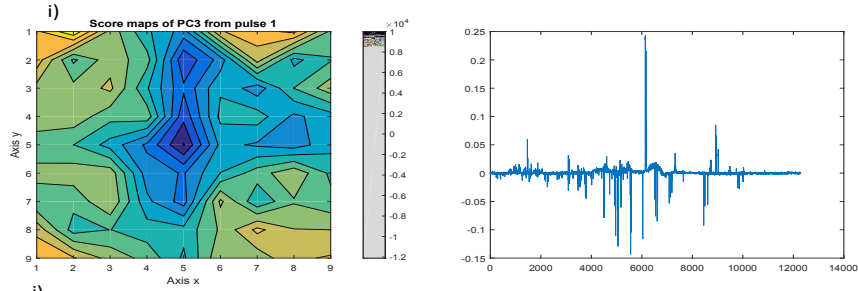


Figure S1. Hyperspectral maps obtained with the experimental runs of design 1 with the respective loading values. a)experimental run 1; b)experimental run 2; c)experimental run 3; d)experimental run 4; e)experimental run 5; f)experimental run 6; g)experimental run 7; h)experimental run 8; i)experimental run 9; j)experimental run 10; k)experimental run 11.





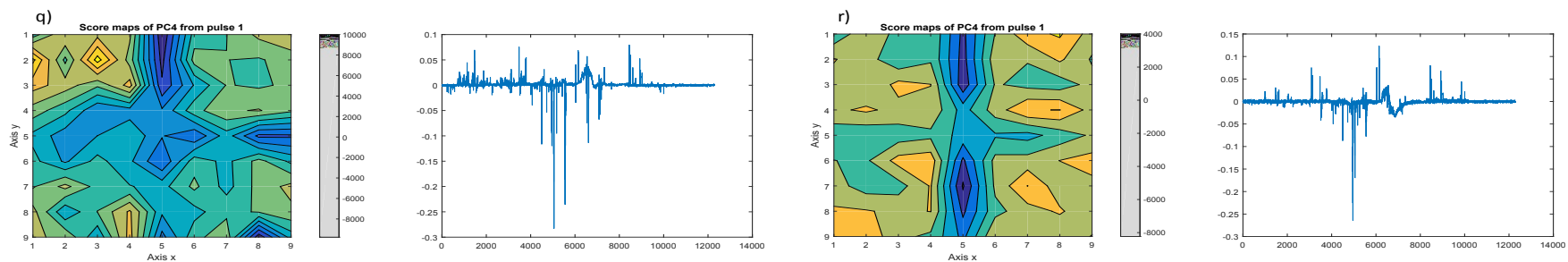


Figure S2. Hyperspectral maps obtained with the experimental runs of design 2 with the respective loading values. a)experimental run 1; b)experimental run 2; c)experimental run 3; d)experimental run 4; e)experimental run 5; f)experimental run 6; g)experimental run 7; h)experimental run 8; i)experimental run 9; j)experimental run 10; k)experimental run 11. l) experimental run 12; m) experimental run 13; n) experimental run 14; o) experimental run 15; p) experimental run 16; r) experimental run 17.

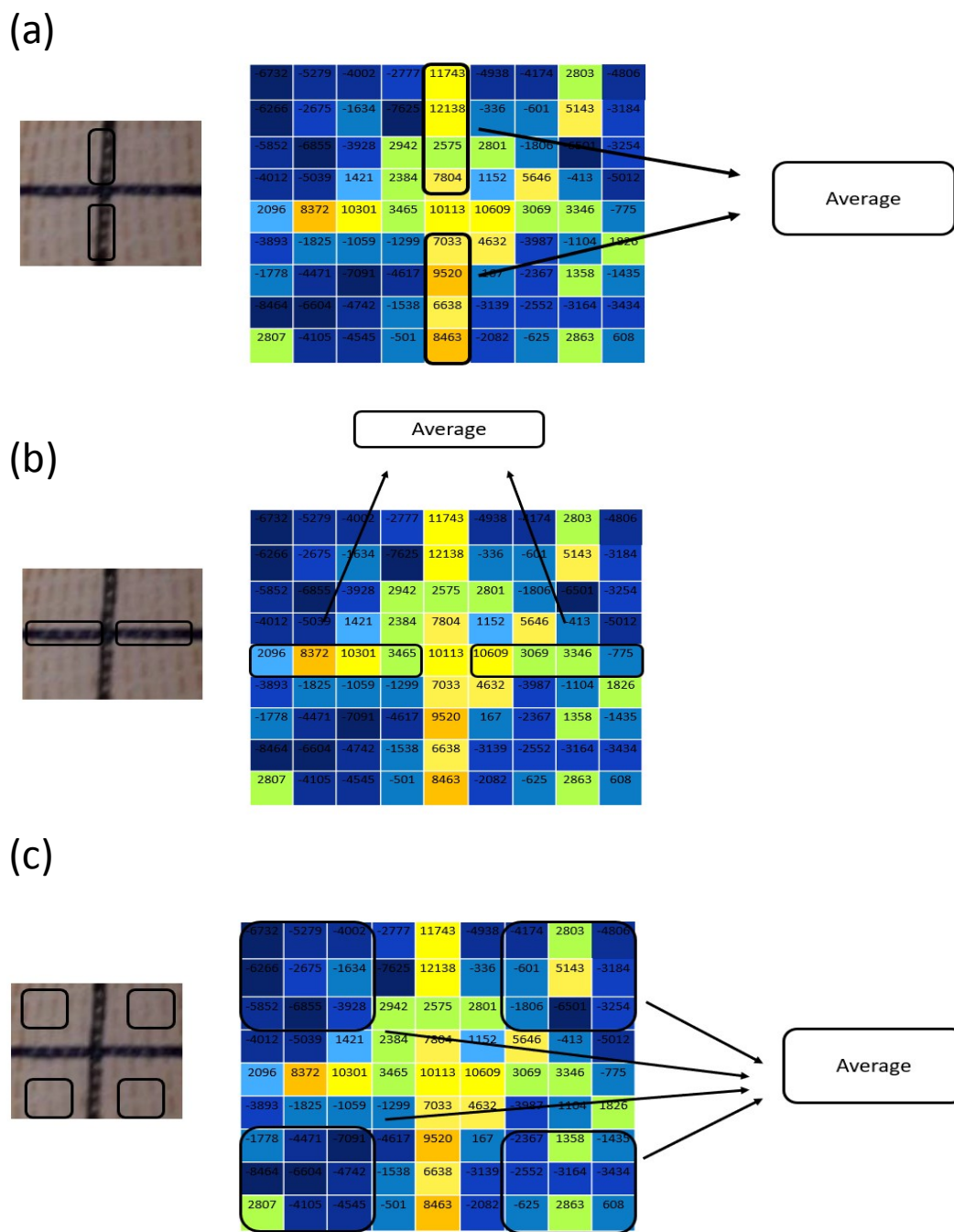


Figure S3. Pictorial description of the data acquisition strategy used in Design 2. a) average score value obtained for the black ink in experimental run 1. b) average score value obtained for the blue ink in experimental run 1. c) average score value obtained for the paper in experimental run 1.

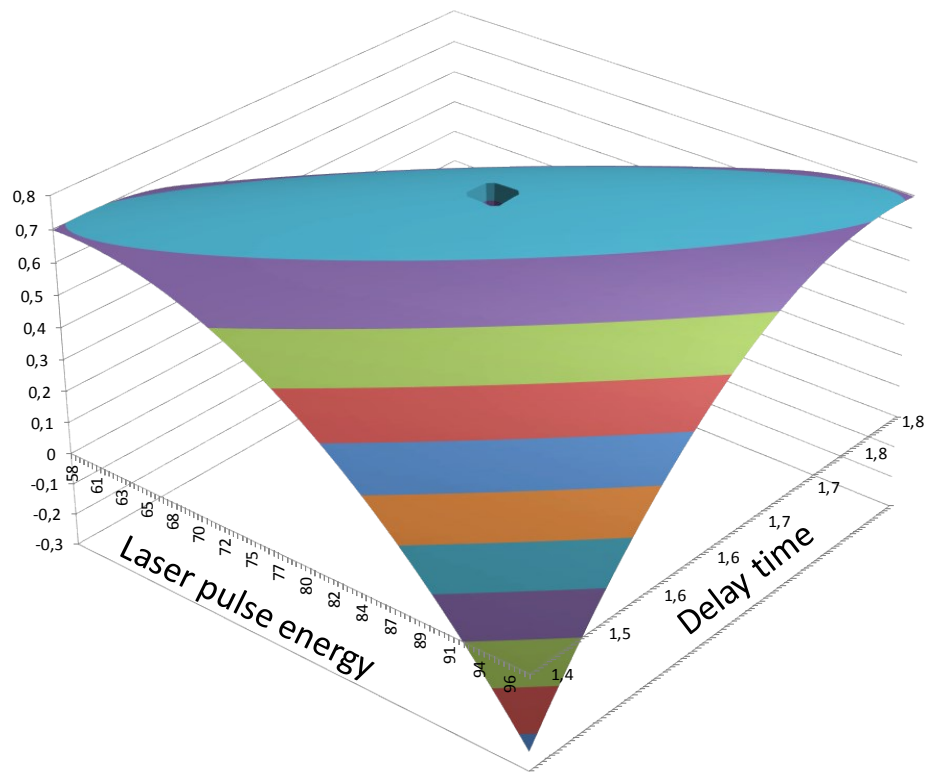


Figure S4. Response surface obtained with the regression model calculated. It is possible to notice that the max D_g is in delay time ~ 1.68 and laser pulse energy $\sim 78\text{mJ}$

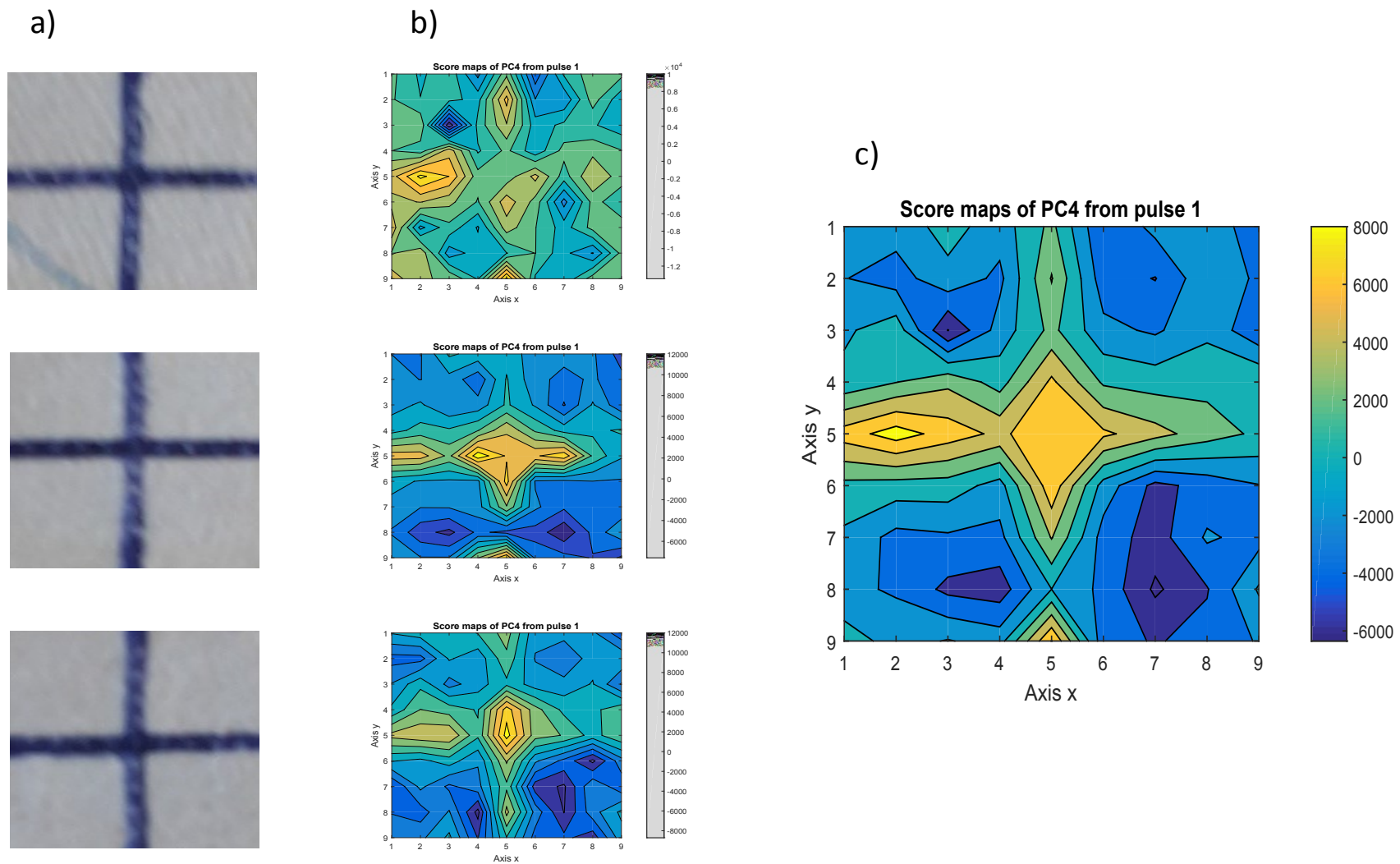
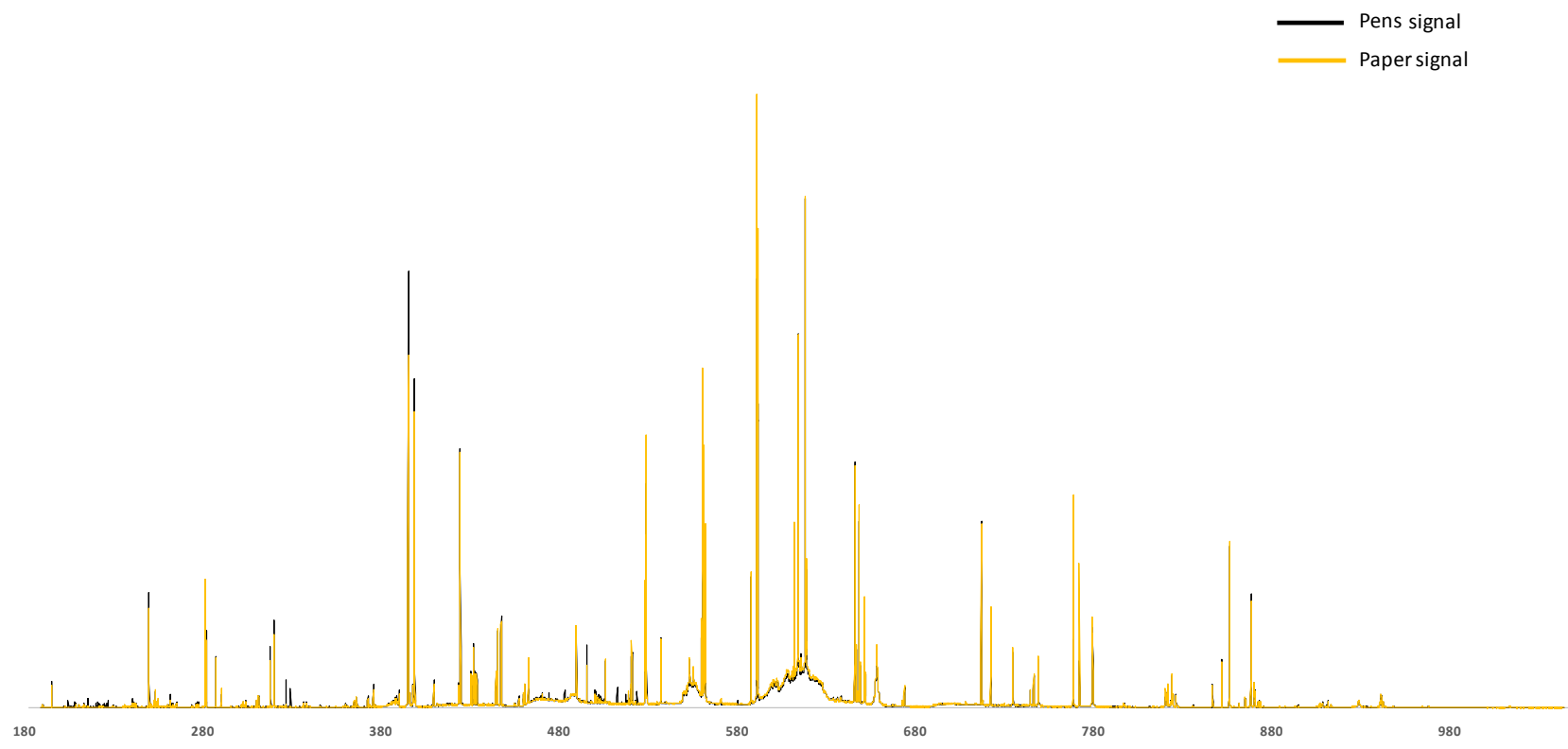


Figure S5. Results obtained for the same color pen test. a) samples; b) hyperspectral maps; c) hyperspectral map obtained with the average signal

a)



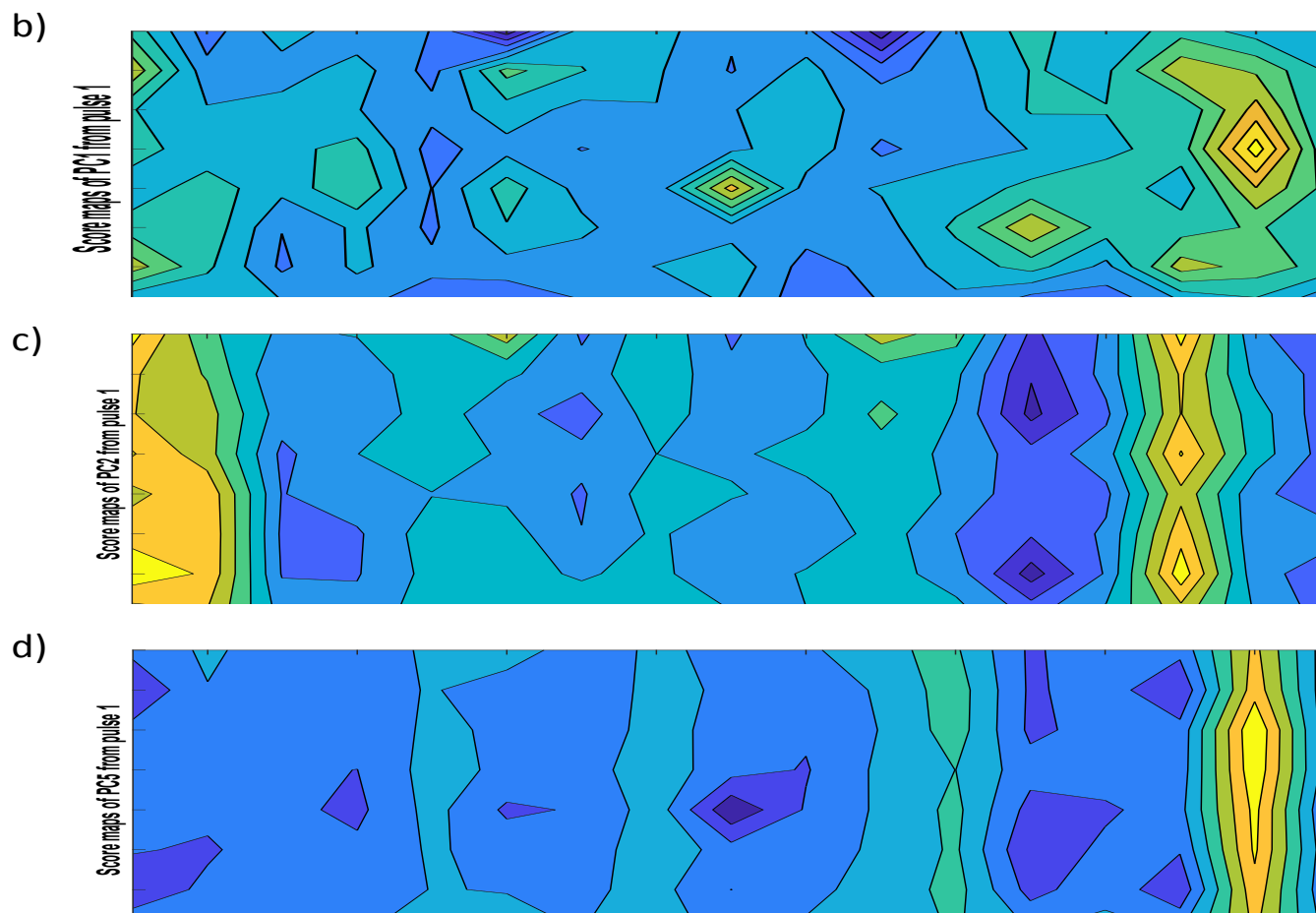
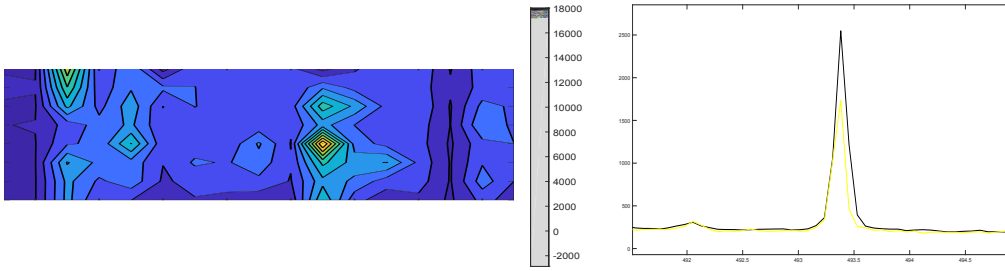
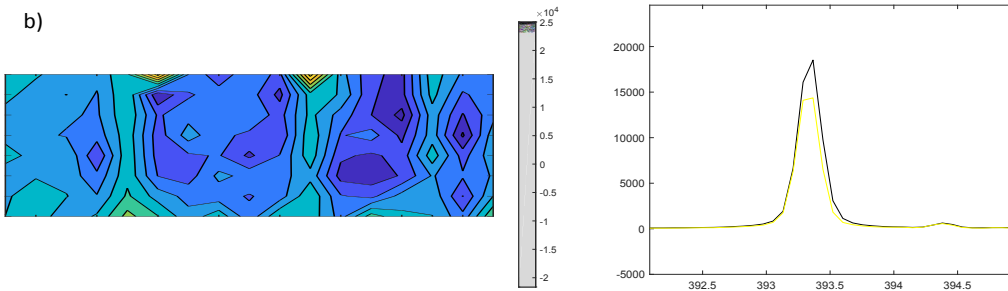


Figure S6. Results obtained for the tests made with all the 16 pens analyzed. a) average spectra obtained for the pens signal in black and for the paper signal in yellow; b) scores map obtained using all the 12288 emission lines for the PC1; c) scores map obtained using all the 12288 emission lines for the PC2; d) scores map obtained using all the 12288 emission lines for the PC5;

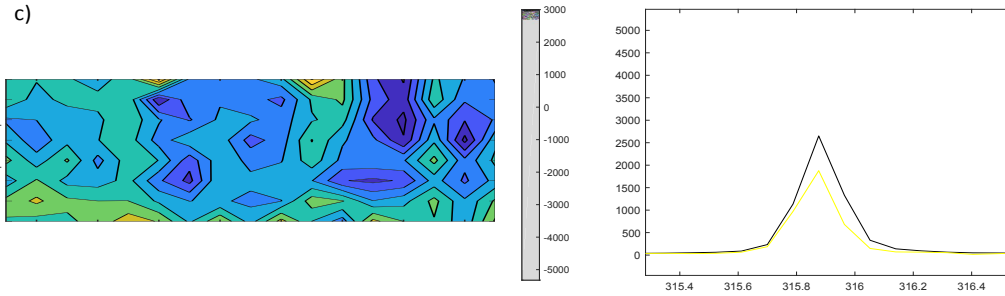
a)



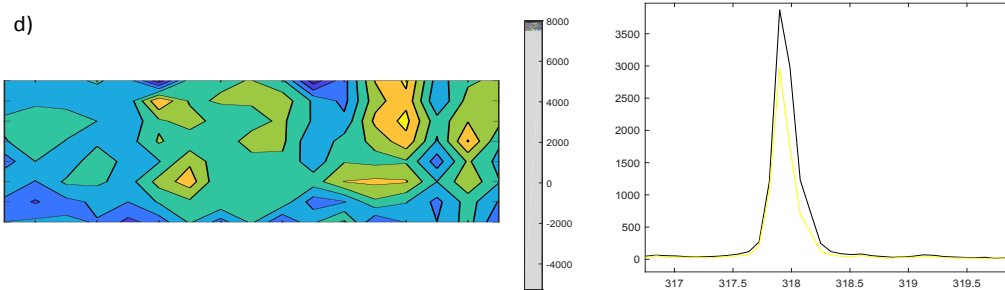
b)



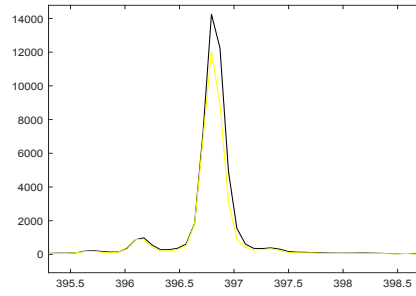
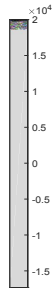
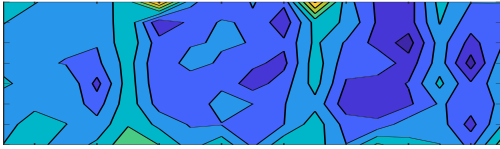
c)



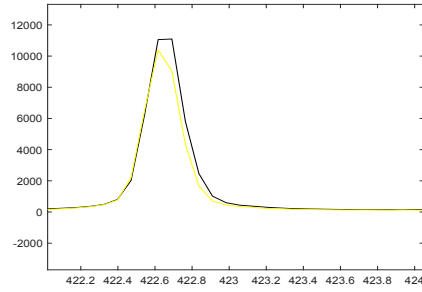
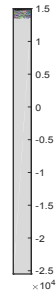
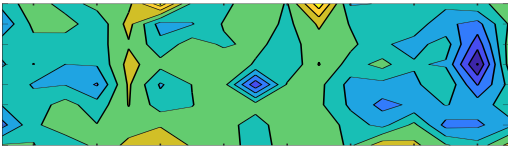
d)



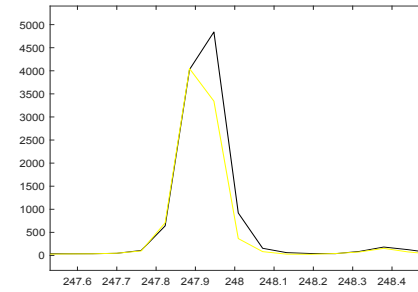
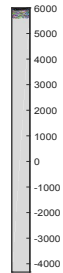
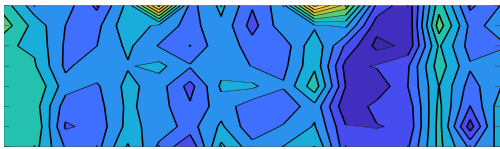
e)



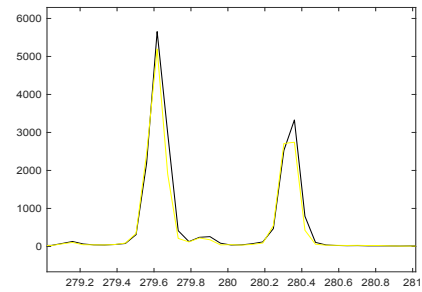
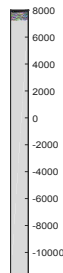
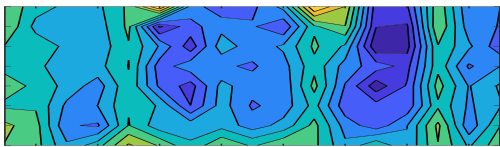
f)



g)



h)



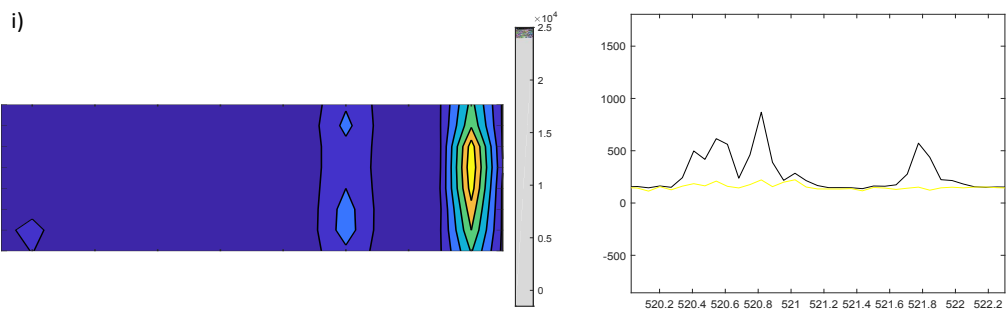
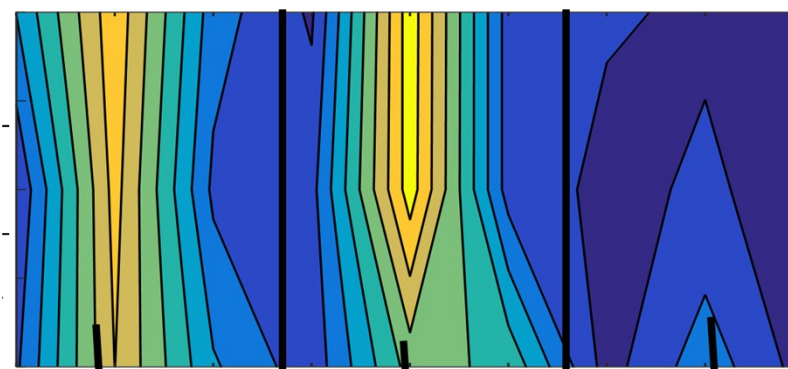


Figure S7.Score map obtained for all the pens in the left and the respective spectral range profile used in the right.



a10 ($3566 \pm 2 \text{ mg kg}^{-1}$) a8 ($291 \pm 2 \text{ mg kg}^{-1}$)



real



real

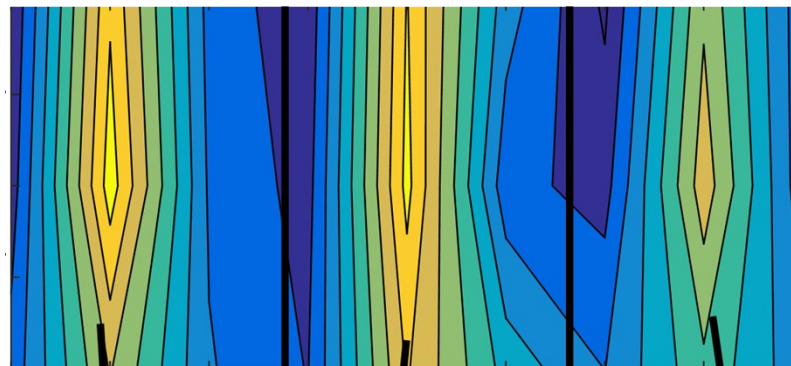


fake

Figure S8. Simulated test of a real situation.



a3 ($2839 \pm 8 \text{ mg kg}^{-1}$) a7 ($2769 \pm 6 \text{ mg kg}^{-1}$)



real

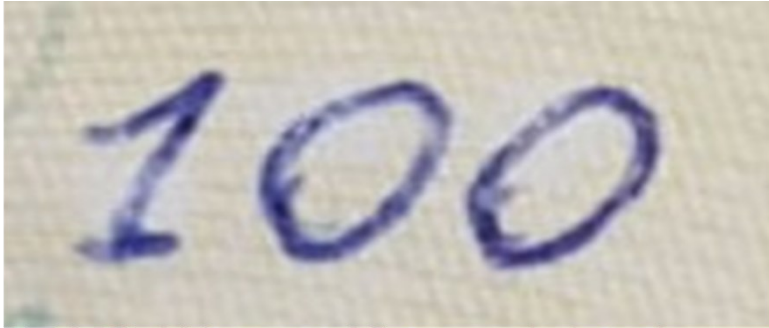


real

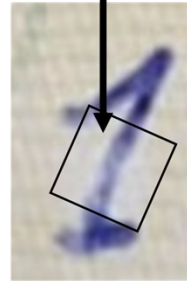
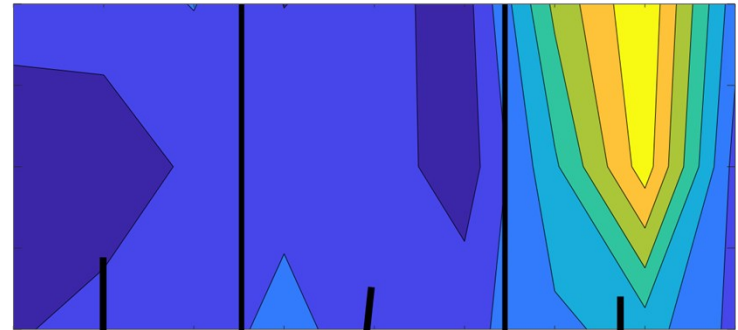


fake

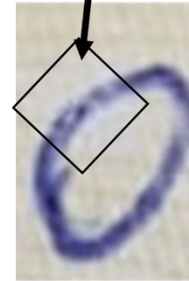
Figure S9. Simulated test of a real situation.



A3 ($2839 \pm 8 \text{ mg kg}^{-1}$) a10 ($3566 \pm 2 \text{ mg kg}^{-1}$)



real



real



fake

Figure S10. Simulated test of a real situation.



A3 ($5744 \pm 27 \text{ mg kg}^{-1}$) a2 ($\text{Cu} < \text{LoD}$)

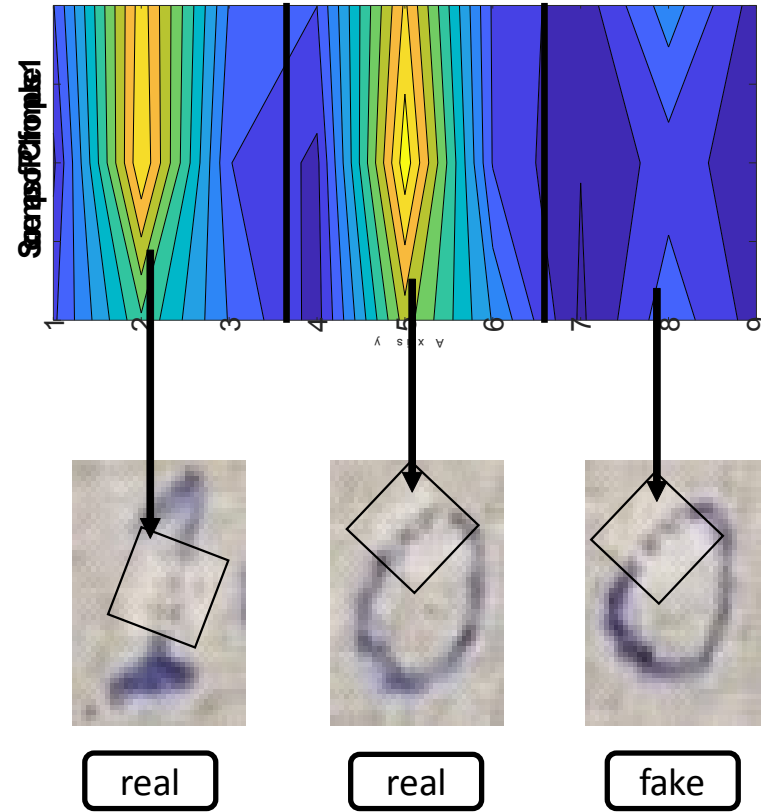


Figure S11. Simulated test of a real situation.