

Supplementary Material

An LC-MS/MS method for quantitation of methylparaben, benzophenone and pharmaceutical compounds from domestic wastewater

Juliana Cristina Barreiro^{1,2*}, Anna Patrícia Florentino³, Izadora Lirano Furlani⁴, Gustavo H. R. Silva¹, Quezia Bezerra Cass⁴

¹Laboratório de Hidráulica e Saneamento, Departamento de Engenharia Civil e Ambiental, Universidade Estadual Paulista, Bauru, SP, Brazil

² Chemistry Institute of São Carlos, University of São Paulo, São Carlos, SP, Brazil

³Laboratory of Microbiology, Wageningen University, Wageningen, The Netherlands

⁴Separare, Departamento de Química, Universidade Federal de São Carlos, São Carlos, SP, Brazil

*** Correspondence:**

Juliana Cristina Barreiro, Quezia Bezerra Cass
juliana.barreiro@gmail.com, qcass@ufscar.br

Table S1. Design for the chromatographic model prediction by DryLab® software.

Run	Samples
1	XSELECT_C18_formate pH 3.0MeOH_ACN50_50_5_95_18
2	XSELECT_C18_acetate pH 4.0MeOH_ACN50_50_5_95_18
3	XSELECT_C18_acetate pH 5.0MeOH_ACN50_50_5_95_18
4	XSELECT_C18_formate pH 3.0MeOH_ACN50_50_5_95_6
5	XSELECT_C18_acetate pH 4.0MeOH_ACN50_50_5_95_6
6	XSELECT_C18_acetate pH 5.0MeOH_ACN50_50_5_95_6

Table S2. Linearity parameters, detection and quantification limits for the method.

Compounds	Range ($\mu\text{g L}^{-1}$)	Calibration equation	R ²	LOD ($\mu\text{g L}^{-1}$)	LOQ ($\mu\text{g L}^{-1}$)
ACM	5.00 - 200	$y=14287.0 + 69.901x$	0.998	$6.25 \cdot 10^{-6}$	5.00
BZN	5.00 - 200	$y=15385.1 + 582.4x$	0.992	0.50	5.00
CBZ	5.00 - 200	$y=13511.7 + 599.1x$	0.997	$6.25 \cdot 10^{-8}$	5.00
NAP	5.00 - 200	$y=11814.71 + 98.241x$	0.994	$2.50 \cdot 10^{-5}$	5.00
PRO	5.00 - 200	$y=467.46 + 330.61x$	0.996	0.50	5.00
AM	5.00 - 200	$y=209.88 + 1636.4x$	0.995	$2.50 \cdot 10^{-3}$	5.00
MET	5.00 - 200	$y=6.268 + 145.86x$	0.998	$4.00 \cdot 10^{-7}$	5.00
EST	250 - 1000	$y=3099.5 + 2.38022x$	0.986	100	250
ESN	250 - 1000	$y=-133.50 + 1.7594x$	0.986	100	250
DIC	100 - 2000	$y=234.83 + 1.1843x$	0.992	50	100
IBU	1000 - 4000	$y=230.17 + 0.0771x$	0.991	100	1000
MEP	50.0 - 500	$y=4.9424 + 4.1118x$	0.984	10	50

Table S3. Accuracy and Intra- and inter-day variability, recovery and matrix effect for the method.

Drugs	QC ($\mu\text{g L}^{-1}$)	Intra-day		Inter-day		Recovery (%)	MEs (%)
		Accuracy (%)	CV (%)	Accuracy (%)	CV (%)		
ACM	6	96.1	9.80	101	9.51	93.9 (2.13)	143
	80	95.8	15.2	110	11.3	98.6 (11.2)	
	160	99.0	19.0	90.7	4.62	96.9 (2.13)	
BZN	6	120	4.18	120	4.16	57.8 (0.38)	95.0
	80	116	6.57	118	13.0	51.2 (11.8)	
	160	102	7.36	110	7.85	40.7 (6.56)	
CBZ	6	91.8	5.21	103	11.5	120 (8.47)	95.6
	80	105	11.0	108	8.48	107 (13.7)	
	160	104	6.79	108	8.37	115 (2.93)	
NAP	6	101	8.82	104	10.6	75.6 (20.2)	84.8
	80	109	13.9	90.5	7.94	87.3 (4.88)	
	160	113	4.58	100	6.29	85.5 (8.54)	
PRO	6	114	8.65	108	6.59	35.5 (6.36)	75.6
	80	101	8.25	110	9.59	38.1 (4.22)	
	160	112	5.28	108	5.90	44.7 (3.21)	
AM	6	87.5	6.13	96.1	13.5	40.6 (10.2)	59.6
	80	101	9.48	100	8.24	34.9 (9.35)	
	160	109	7.84	111	6.40	59.7 (1.23)	
MET	6	108	2.56	108	3.30	74.3 (8.23)	159
	80	114	9.10	89.3	17.9	70.9 (5.45)	
	160	110	6.25	111	6.76	77.3 (7.30)	
EST	300	89.9	7.42	86.0	13.3	37.5 (3.74)	113
	400	112	5.54	111	4.87	33.4 (2.40)	
	800	95.8	14.9	95.4	14.6	43.5 (4.91)	

ESN	300	111	4.52	112	3.44	40.6 (0.12)	104
	400	116	4.64	115	5.62	90.2 (16.1)	
	800	107	8.95	111	5.85	68.9 (11.6)	
DIC	120	88.0	6.82	99.3	13.9	59.8 (14.2)	82.0
	800	102	8.93	104	9.41	56.7 (20.0)	
	1000	90.4	7.67	101	11.4	50.6 (3.38)	
IBU	1200	110	3.63	104	12.2	59.0 (0.85)	115
	2400	103	17.4	104	12.8	85.1 (4.32)	
	3200	112	7.51	109	8.66	102 (14.9)	
MEP	60	96.9	13.2	95.9	12.4	66.0 (1.50)	101
	250	115	6.36	111	6.23	68.9 (13.6)	
	375	112	8.02	109	8.55	43.1 (8.3)	

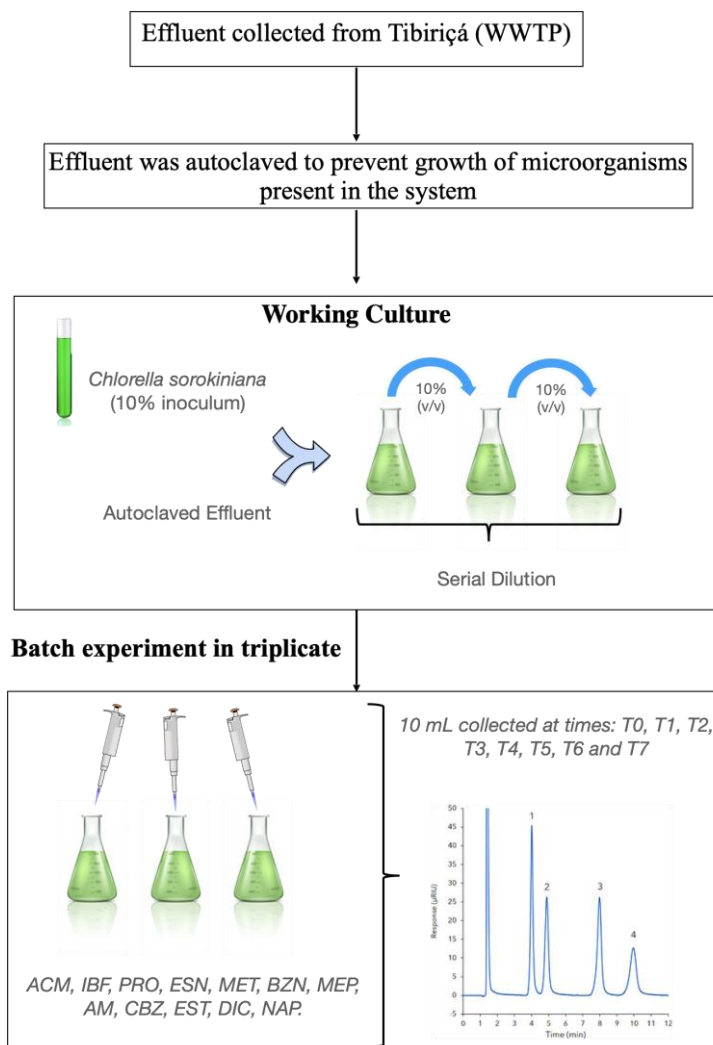


FIGURE S1. Schematic workflow for bioremediation of domestic wastewater samples by microalgae culture.

Resolution Map for the Selected Working Point

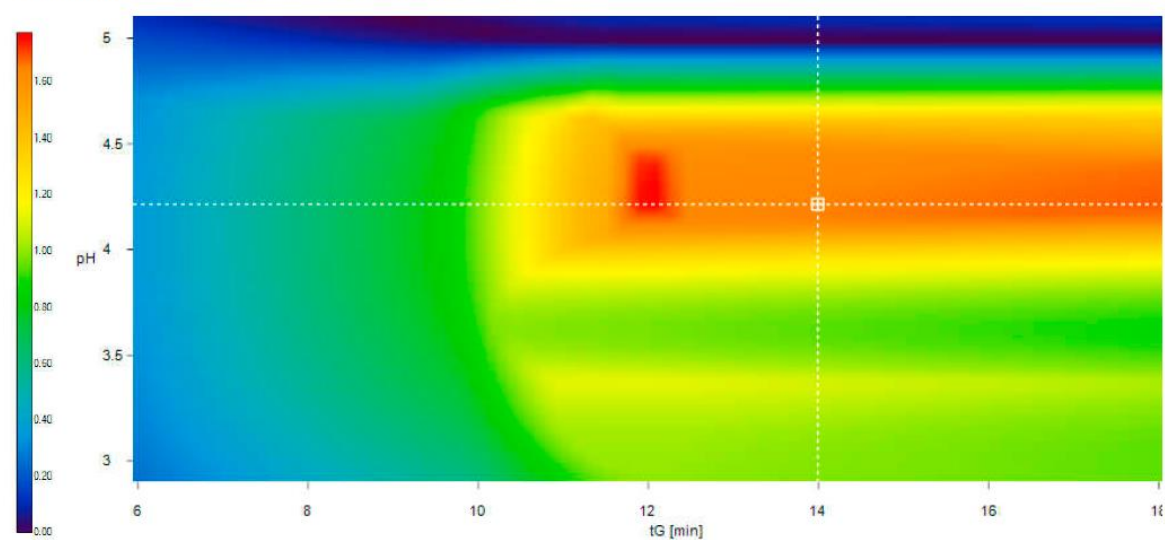


FIGURE S2. 2D resolution map for pH and t_G variables.

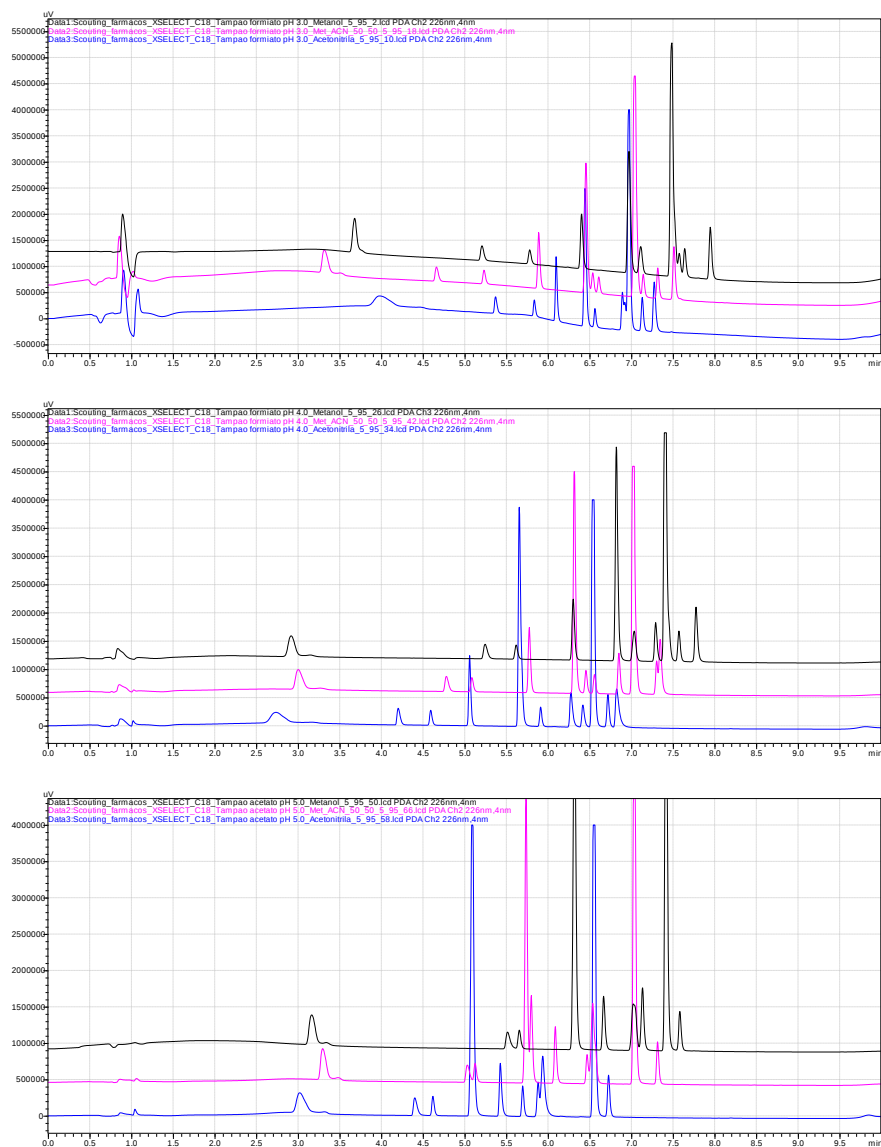
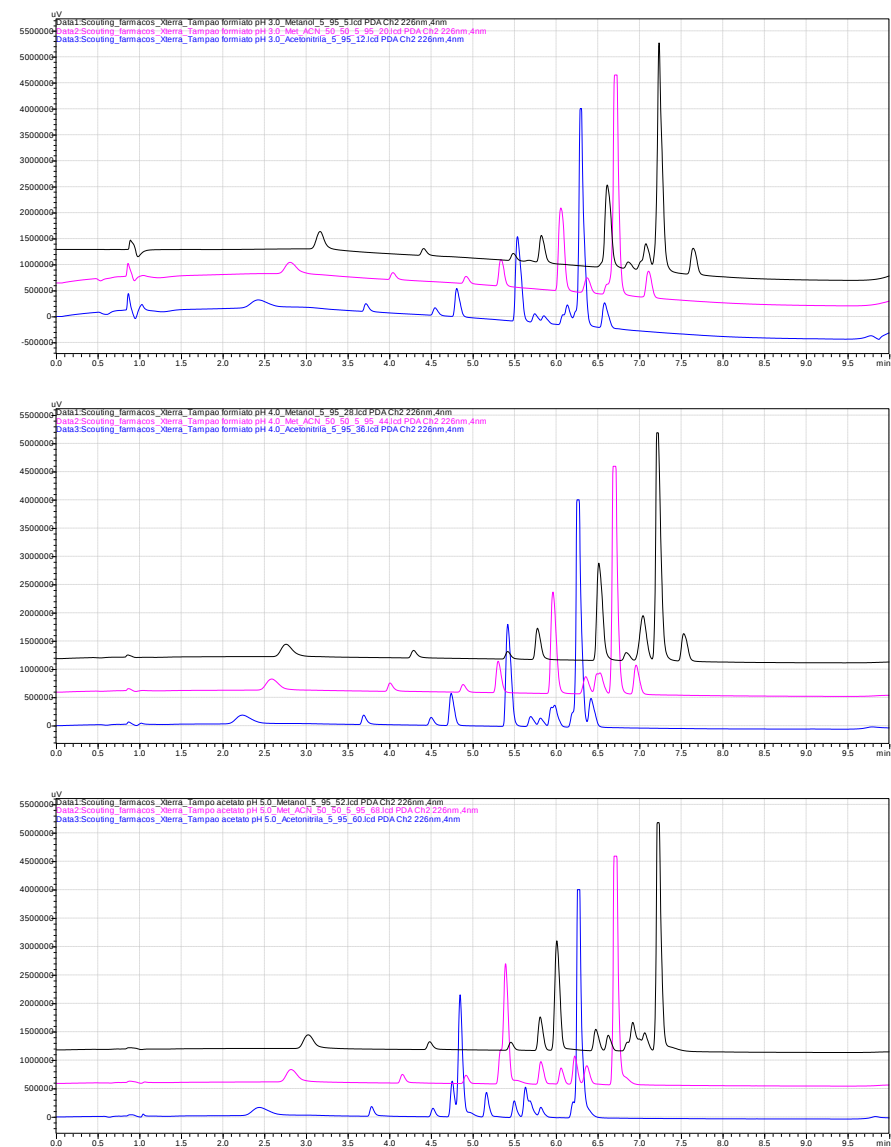
(A)**(B)**

FIGURE S3. Chromatograms obtained for the analyzes in exploratory gradient from 5 to 95%B in 6 min (A) - XSelect® CSH and (B) – Xterra® column at different pHs and mobile phase compositions.

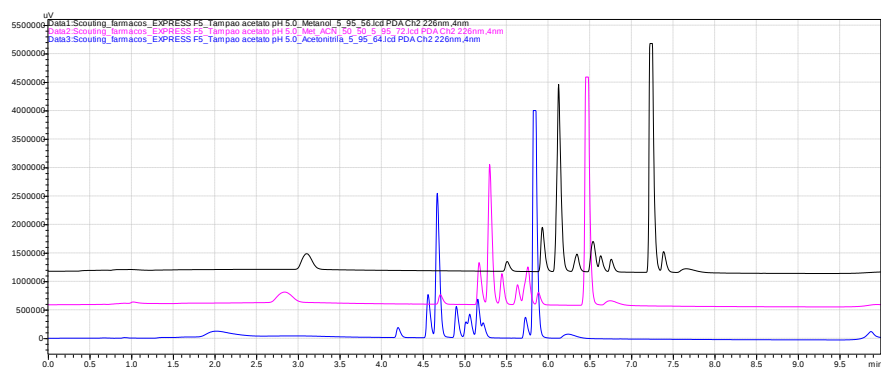
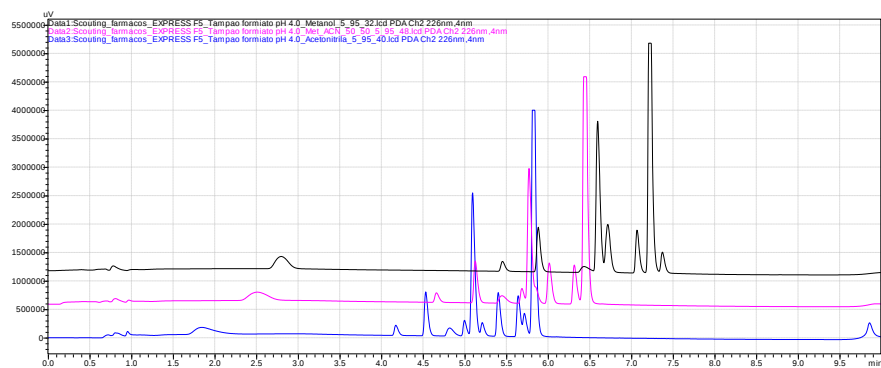
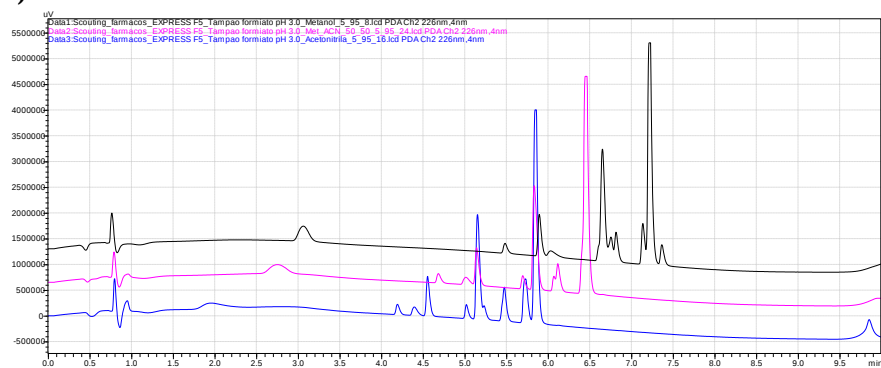
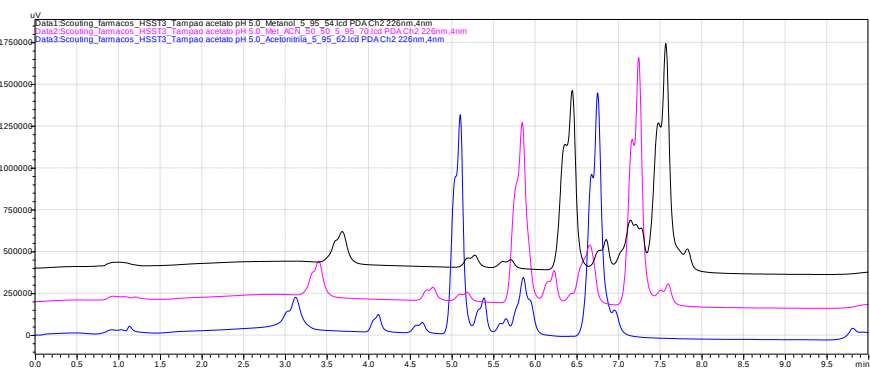
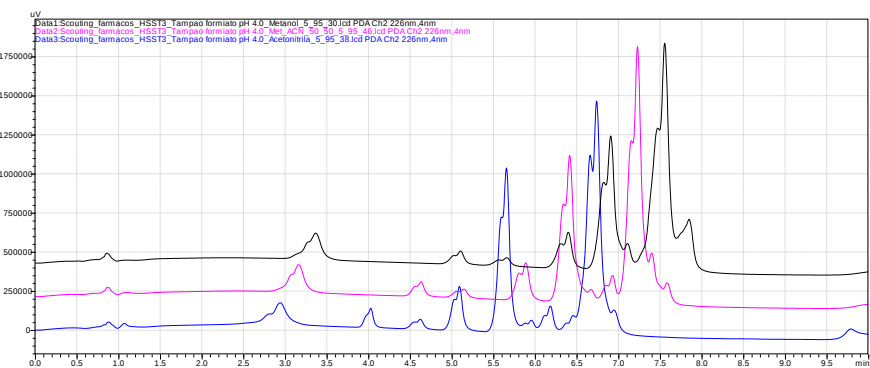
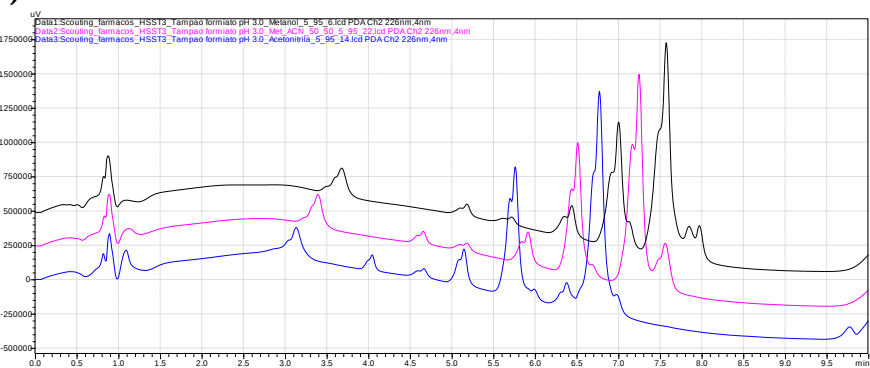
(A)**(B)**

FIGURE S4. Chromatograms obtained for the analyzes in exploratory gradient from 5 to 95%B in 6 min (A) - Ascentis® Express F5 and (B) XSelect® HSST3column at different pHs and mobile phase compositions.

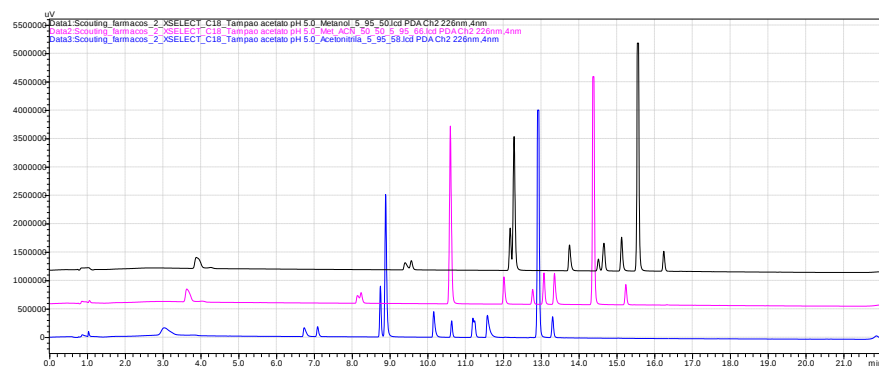
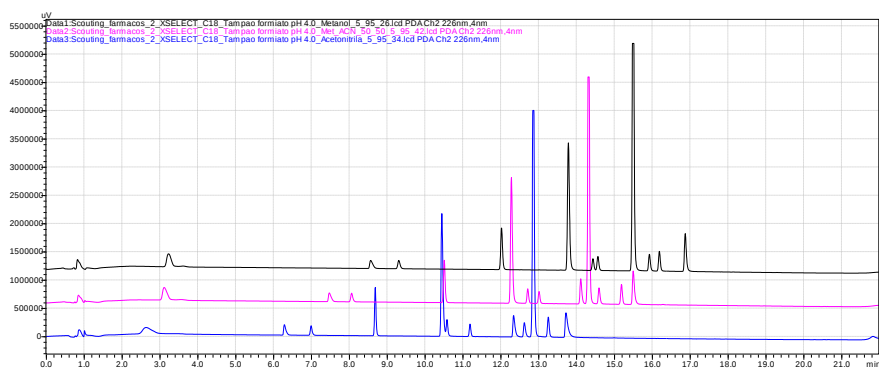
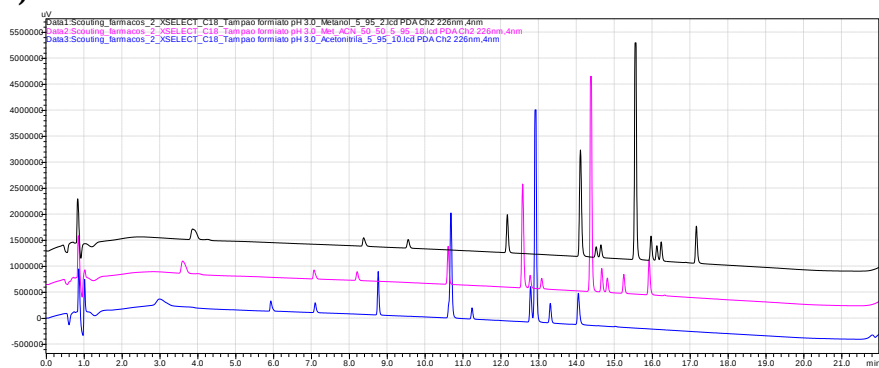
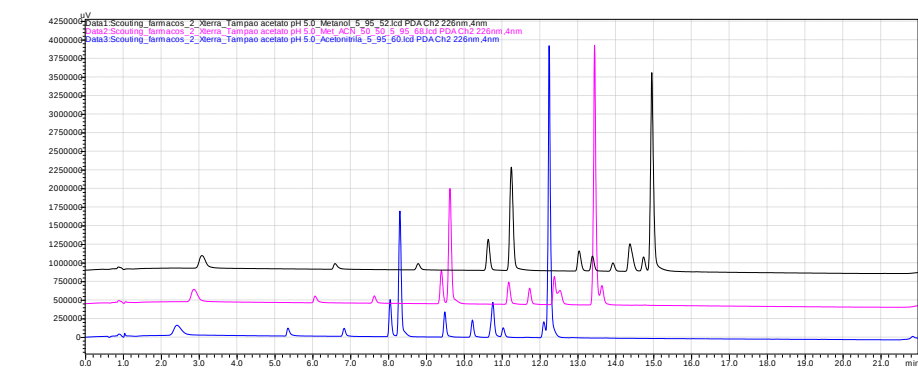
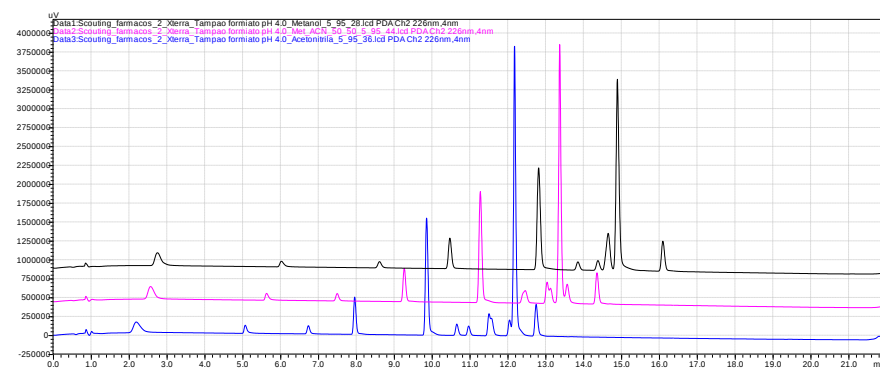
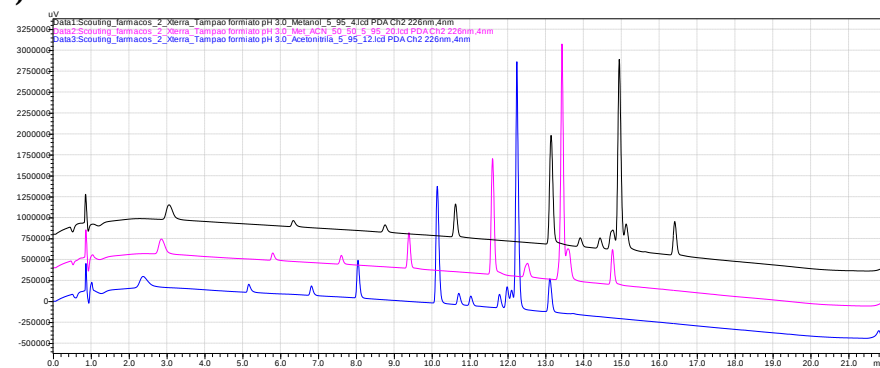
(A)**(B)**

FIGURE S5. Chromatograms obtained for the analyzes in exploratory gradient from 5 to 95%B in 18 min (A) - XSelect® CSH and (B) – Xterra® column at different pHs and mobile phase compositions.

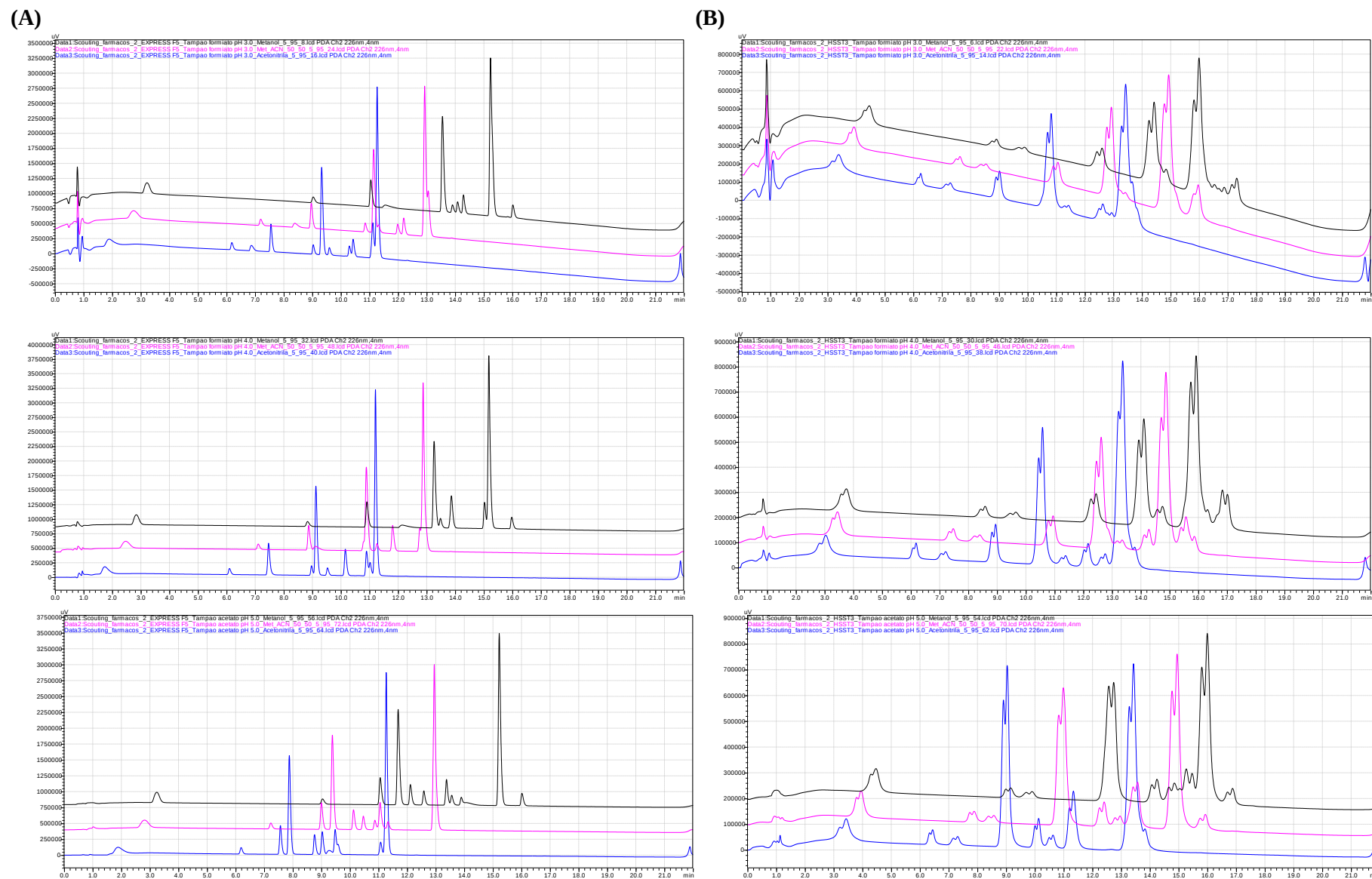


FIGURE S6. Chromatograms obtained for the analyzes in exploratory gradient from 5 to 95%B in 18 min (A) - Ascentis® Express F5 and (B) XSelect® HSST3 column at different pHs and mobile phase compositions.