

A rational strategy based on experimental designs to optimize parameters of a liquid chromatography-mass spectrometry analysis of complex matrices

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Supplementary information

Figure S1 : Key parameters for ESI detection optimized with DoE (red boxed text) and before DoE (purple boxed text)

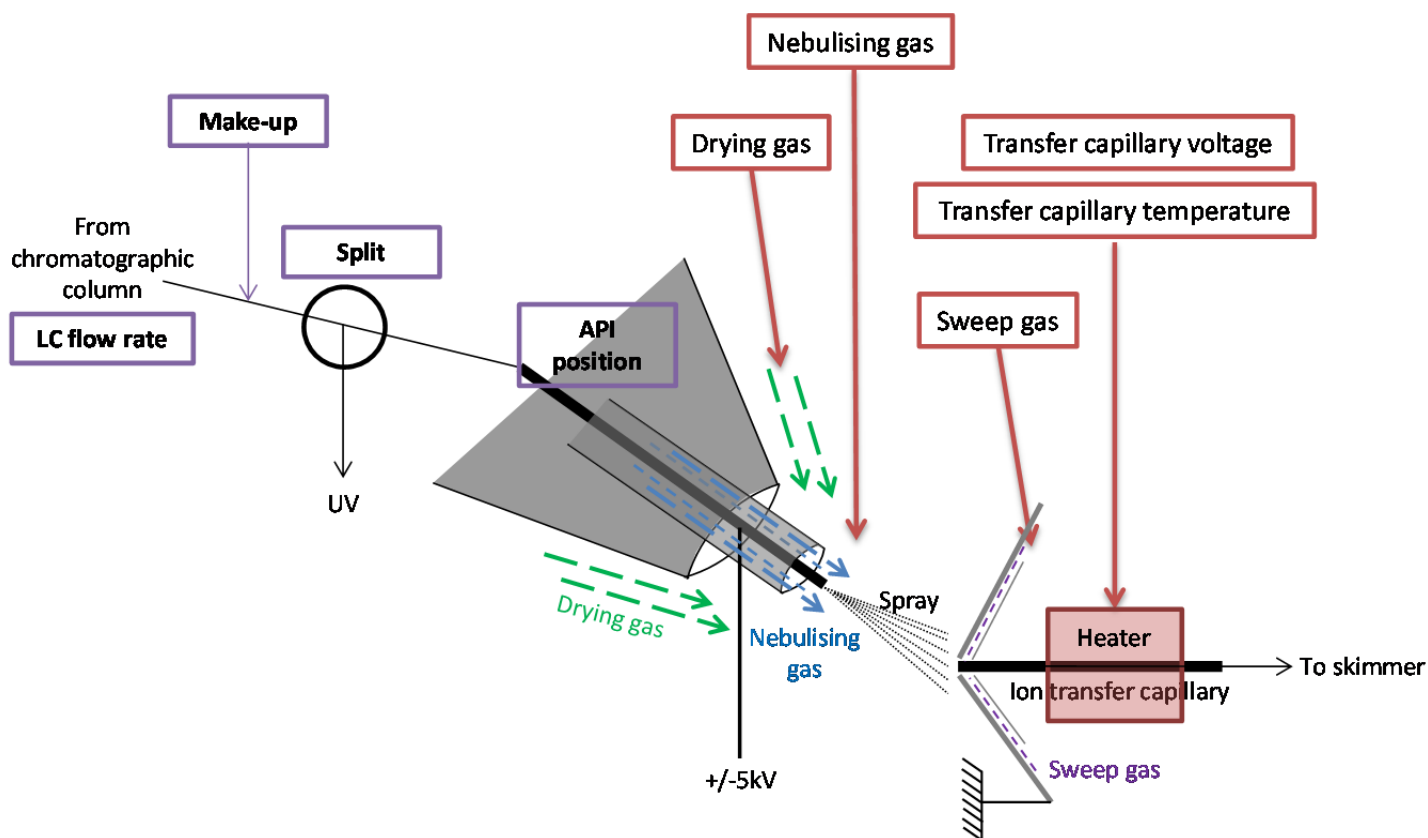
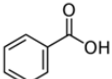

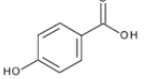
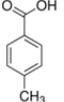

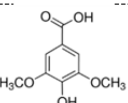
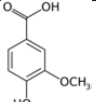
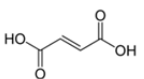

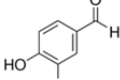
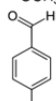



Table S1: Model mixtures for negative-ion (left) and positive-ion (right) modes

Model compound	Structure	pKa
Benzoic acid		4.08
3-hydroxybenzoic acid		3.84 / 9.55
4-hydroxybenzoic acid		4.38 / 9.67
p-toluic acid		4.26
o-toluic acid		3.96
Syringic acid		3.93 / 9.55
Vanillic acid		4.16 / 10.14
Fumaric acid		3.35 / 4.22
Stearic acid		4.95
Vanillin		7.81
4-hydroxybenzaldehyde		7.32
Benzaldehyde		>12

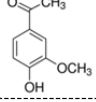

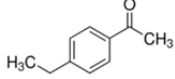
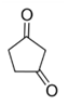
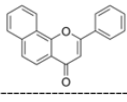
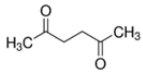
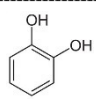

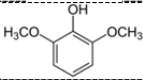
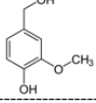
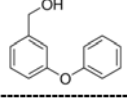
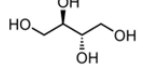
Model compound	Structure	pKa
Acetovanillone		8.27
Acetophenone		>12
4-ethylacetophenone		>12
1,3-cyclopentadione		8.29
α-naphthoflavone		>12
2,5-hexanedione		>12
Catechol		9.34 / 12.79
Guaiacol		9.98
Syringol		9.37
Vanillyl alcohol		9.92 / 15.13
(3-phenoxyphenyl)methanol		14.91
Erythritol		13.04 / 14.29 / 15.40

Figure S2: Percentage of remaining plates according to the split ratio

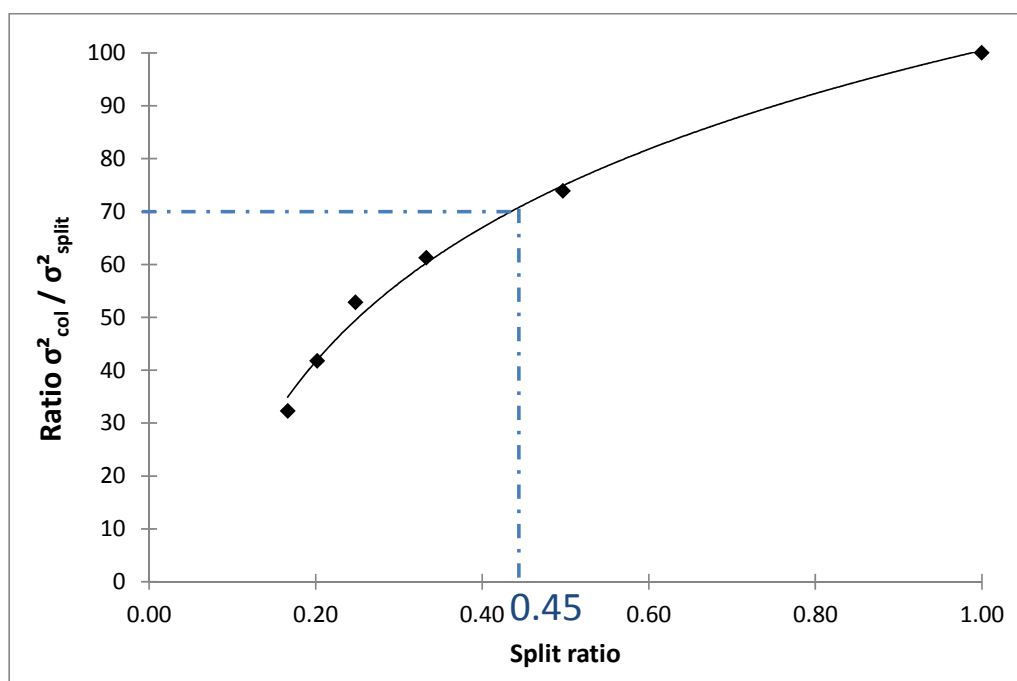
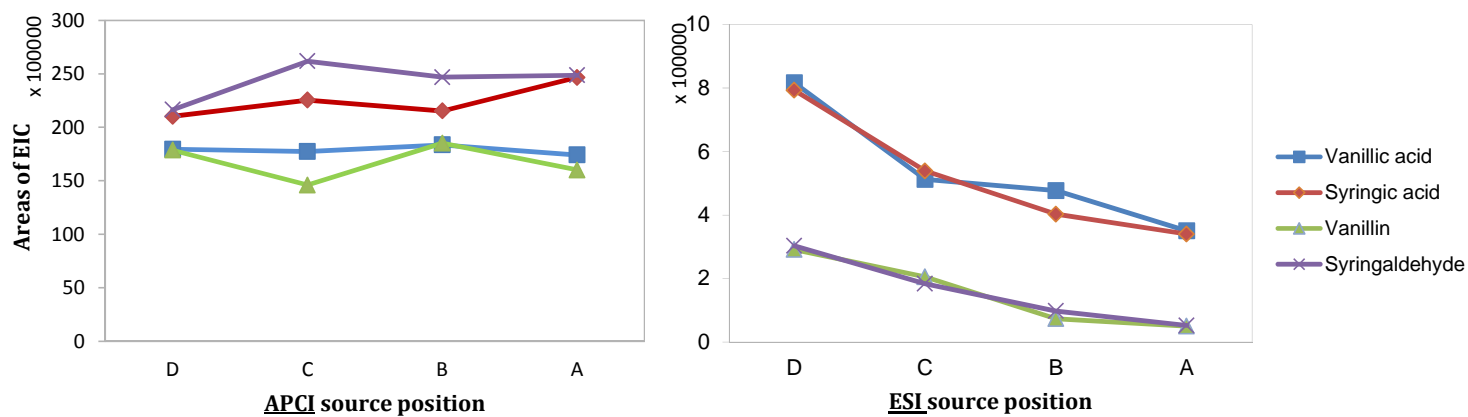


Figure S3: Areas of EIC for 4 model compounds according to the ESI and APCI position (negative-ion mode). [LC and MS conditions : see Experimental part]



For the designs of experiments, each measure was repeated 3 times (5 for the center points). These replicates allowed to calculate the variances which are presented in Table S2, S3, S4 and S5. When no signal could be measure during the three replicates, the variance could not be calculated and is represented with a slash (/) in the following tables. Variances above 30% are indicated in red.

Table S2: Variances in percentage of the performed measurements during the design of experiments for (-)ESI

A: sheath gas (AU)	B: auxiliary gas (AU)	C: sweep gas (AU)	D: capillary temperature (°C)	E: capillary voltage (V)	Fumaric acid	4-hydroxybenzoic acid	4-hydroxybenzaldehyde	3-hydroxybenzoic acid	Vanillic acid	Vanilin	Syringic acid	Benzaldehyde	Benzoic acid	o-toluic acid	p-toluic acid	Stearic acid
19	6	6	222	64	/	21	12	12	2	4	3	/	/	/	/	6
31	6	6	222	64	/	10	24	24	6	6	5	/	/	173	/	12
19	14	6	222	64	173	9	30	8	12	1	5	/	/	/	/	3
31	14	6	222	64	41	2	27	21	11	14	12	/	/	89	/	24
19	6	14	222	64	/	11	4	56	2	7	1	/	/	173	/	1
31	6	14	222	64	/	5	4	23	2	6	1	/	/	18	88	1
19	14	14	222	64	/	2	20	58	2	3	1	/	/	45	/	2
31	14	14	222	64	/	4	5	23	6	2	1	/	/	10	28	1
19	6	6	298	64	17	1	6	3	4	3	4	82	91	13	36	4
31	6	6	298	64	18	3	3	3	6	3	3	50	16	2	20	4
19	14	6	298	64	16	14	16	27	25	15	18	54	85	26	35	42
31	14	6	298	64	3	3	4	1	4	6	7	10	13	4	5	4
19	6	14	298	64	9	1	3	3	3	2	2	23	31	19	21	15
31	6	14	298	64	4	5	1	5	2	3	1	4	5	1	4	7
19	14	14	298	64	10	13	11	20	22	10	19	30	28	22	31	39
31	14	14	298	64	7	6	1	3	1	2	2	3	9	4	2	5
19	6	6	222	86	/	6	11	7	5	6	4	/	/	13	/	10
31	6	6	222	86	173	8	14	17	6	0	5	/	/	87	118	9
19	14	6	222	86	/	8	1	13	7	2	4	/	/	48	/	2
31	14	6	222	86	/	3	5	7	7	4	7	/	/	17	20	7
19	6	14	222	86	/	4	3	9	3	2	3	/	/	15	77	1

31	6	14	222	86	10	2	5	4	4	5	1	9	/	9	5	4
19	14	14	222	86	/	4	4	2	6	6	2	25	/	7	37	6
31	14	14	222	86	101	2	2	9	1	3	2	21	/	3	2	1
19	6	6	298	86	2	8	5	5	5	4	4	3	6	3	7	5
31	6	6	298	86	10	4	1	4	10	5	6	2	6	3	4	3
19	14	6	298	86	8	6	2	2	3	4	2	21	16	2	7	13
31	14	6	298	86	7	2	2	1	1	3	1	3	4	3	3	4
19	6	14	298	86	7	3	3	1	2	4	1	1	2	2	0	2
31	6	14	298	86	15	4	3	2	2	2	2	2	0	4	5	7
19	14	14	298	86	8	2	2	3	4	4	1	6	4	6	1	2
31	14	14	298	86	13	1	3	3	3	1	2	4	1	1	8	15
10	10	10	260	75	95	11	16	14	4	3	2	/	/	15	35	22
40	10	10	260	75	14	3	11	5	5	6	7	11	/	5	21	1
25	0	10	260	75	21	8	3	8	14	2	1	/	/	13	173	19
25	20	10	260	75	43	3	3	10	4	3	2	73	19	13	27	7
25	10	0	260	75	173	7	4	10	5	3	2	/	/	35	/	14
25	10	20	260	75	22	2	3	3	3	1	7	29	89	9	9	6
25	10	10	170	75	/	9	88	100	7	14	12	/	/	/	/	16
25	10	10	350	75	5	3	3	4	1	1	2	0	3	7	4	5
25	10	10	260	50	/	6	12	29	8	4	4	/	/	27	173	10
25	10	10	260	100	10	4	4	3	9	2	3	7	10	5	3	1
25	10	10	260	75	57	6	5	7	3	5	5	120	/	8	26	2

Table S3: Variances in percentage of the performed measurements during the design of experiments for (+)ESI

A: sheath gas (AU)	B: auxiliary gas (AU)	C: sweep gas (AU)	D: capillary temperature (°C)	E: capillary voltage (V)	Erythritol	1,3-cyclopentanedi one	Catechol	2,5-hexanedi one	Vanillyl alcohol	Guaiacol	Aceto-vanillone	Syringol	Aceto-pheno ne	4-ethyl acetophen one	(3-phenoxyphenyl) methanol	Naphtoflav one
10	0	0	200	50	173	/	/	/	/	15	41	173	/	/	/	17
36	0	0	200	50	/	173	102	22	48	12	20	32	/	32	40	13
10	24	0	200	50	/	/	/	39	5	4	10	10	87	7	2	5
36	24	0	200	50	/	71	10	5	8	5	4	4	9	3	3	5
10	0	14	200	50	/	/	/	10	21	5	6	6	70	7	5	6
36	0	14	200	50	16	66	5	3	4	4	2	6	64	5	2	5
10	24	14	200	50	/	/	/	2	8	2	3	6	11	6	3	5
36	24	14	200	50	67	23	5	1	3	3	4	4	5	3	1	4
23	12	7	200	80	173	104	105	6	4	4	8	3	91	8	3	35
10	0	0	200	110	/	/	/	/	138	52	46	38	/	173	173	29
36	0	0	200	110	173	33	8	4	7	5	7	5	/	33	29	17
10	24	0	200	110	/	/	/	173	28	18	38	27	95	13	8	5
36	24	0	200	110	/	7	20	10	4	0	1	1	173	3	1	1
10	0	14	200	110	/	/	/	/	13	1	3	5	/	3	3	3
36	0	14	200	110	8	3	10	4	2	3	3	2	119	2	1	5
10	24	14	200	110	/	/	173	/	7	4	10	8	88	8	13	6
36	24	14	200	110	38	41	24	12	1	2	1	4	18	2	1	4
23	12	7	280	50	7	19	17	8	3	7	2	7	3	6	6	15
23	12	0	280	80	10	11	/	6	2	1	2	4	18	2	3	1
23	0	7	280	80	22	12	96	13	4	2	1	8	32	2	2	4
10	12	7	280	80	/	/	/	/	7	5	3	1	10	4	4	2
23	12	7	280	80	79	14	/	10	4	6	2	4	6	4	8	7
36	12	7	280	80	2	18	36	7	3	4	2	1	7	4	5	6
23	24	7	280	80	/	53	/	9	6	5	1	1	19	2	1	3
23	12	14	280	80	/	11	/	19	1	2	1	4	10	1	6	3
23	12	7	280	110	/	173	173	/	2	4	4	8	/	2	/	12
10	0	0	360	50	/	28	173	46	34	3	22	14	100	3	3	4

36	0	0	360	50	8	11	62	36	8	7	2	15	8	3	9	11
10	24	0	360	50	/	/	/	173	6	13	18	9	10	9	15	13
36	24	0	360	50	4	13	/	4	1	3	1	2	5	3	8	2
10	0	14	360	50	/	/	/	/	24	3	11	8	14	1	5	5
36	0	14	360	50	1	3	/	9	6	2	2	5	7	3	2	4
10	24	14	360	50	/	/	173	/	36	6	12	6	10	2	9	9
36	24	14	360	50	12	7	/	6	2	2	1	1	6	2	1	4
23	12	7	360	80	/	128	/	/	38	31	46	47	108	9	173	7
10	0	0	360	110	173	/	/	/	58	43	75	98	/	42	/	8
36	0	0	360	110	/	/	/	/	92	62	76	173	/	95	/	35
10	24	0	360	110	/	/	/	/	/	118	/	/	/	88	/	24
36	24	0	360	110	173	/	/	/	173	48	173	/	/	/	/	6
10	0	14	360	110	/	/	/	/	/	173	/	/	/	/	/	2
36	0	14	360	110	/	/	/	173	/	2	/	/	173	/	/	9
10	24	14	360	110	/	/	/	/	/	/	/	/	/	/	/	17
36	24	14	360	110	/	/	/	173	/	36	/	/	/	/	/	4

Table S4: Variances in percentage of the performed measurements during the design of experiments for (-)APCI

A: sheath gas (AU)	B: auxiliary gas (AU)	C: capillary temperature (°C)	D: capillary voltage (V)	E: vaporizer temperature (°C)	Fumaric acid	4-hydroxy benzoic acid	4-hydroxy benzaldehyde	3-hydroxy benzoic acid	Vanillic acid	Vanillin	Syringic acid	Benzaldehyde	Benzoic acid	o-toluic acid	p-toluic acid	Stearic acid
10	10	250	20	250	/	52	12	/	16	8	2	/	/	/	/	123
50	10	250	20	250	/	31	15	/	33	20	23	88	/	/	/	173
10	40	250	20	250	/	6	9	/	13	15	17	/	/	/	/	2
50	40	250	20	250	/	2	18	/	17	15	19	/	/	/	/	14
10	10	250	50	250	/	12	1	33	19	4	13	/	/	19	/	18
50	10	250	50	250	123	13	6	3	13	6	7	/	/	52	/	8
10	40	250	50	250	45	1	14	13	23	6	35	/	/	31	45	10
50	40	250	50	250	15	5	9	12	2	5	5	/	/	10	87	8
30	25	250	35	350	9	8	5	13	4	5	3	/	/	10	91	7
10	10	250	20	450	173	29	29	26	18	8	24	22	37	9	27	29
50	10	250	20	450	36	5	1	7	4	1	3	87	/	5	27	2
10	40	250	20	450	25	10	9	11	18	5	11	6	20	7	8	10
50	40	250	20	450	24	7	3	10	3	19	4	11	/	3	24	4
10	10	250	50	450	33	36	22	23	25	12	20	11	12	6	10	4
50	10	250	50	450	8	2	3	4	6	1	4	21	7	23	2	9
10	40	250	50	450	6	42	28	35	37	18	30	21	26	16	22	36
50	40	250	50	450	12	3	5	1	4	2	4	4	5	3	8	3
30	25	350	35	250	9	3	1	3	1	1	2	16	7	4	9	5
30	25	350	20	350	3	2	5	6	2	2	8	16	9	6	5	1
30	10	350	35	350	8	4	3	2	1	1	1	4	9	2	2	4
10	25	350	35	350	36	11	32	25	34	12	25	26	12	8	7	6
30	25	350	35	350	8	2	2	2	3	3	5	5	1	3	4	8
50	25	350	35	350	5	2	3	2	2	2	1	4	5	5	3	13
30	40	350	35	350	2	2	2	26	3	3	3	3	3	6	3	6
30	25	350	50	350	13	3	1	2	4	3	3	1	5	2	1	8
30	25	350	35	450	5	2	2	1	2	2	2	3	2	3	8	6
10	10	450	20	250	28	2	7	7	10	2	6	4	3	3	10	14

50	10	450	20	250	2	4	2	4	5	0	3	4	2	3	8	2
10	40	450	20	250	18	7	6	14	4	5	6	6	3	8	9	15
50	40	450	20	250	18	4	2	1	2	3	6	8	1	0	3	3
10	10	450	50	250	/	5	6	10	4	8	9	35	10	16	10	4
50	10	450	50	250	/	0	4	0	3	4	1	7	91	16	23	8
10	40	450	50	250	/	22	3	/	8	8	7	/	/	/	/	27
50	40	450	50	250	/	9	74	9	5	1	3	173	/	/	/	4
30	25	450	35	350	14	2	1	2	2	2	1	7	2	5	4	11
10	10	450	20	450	16	1	11	10	8	14	5	3	2	12	3	9
50	10	450	20	450	4	1	4	3	3	2	3	3	3	6	0	13
10	40	450	20	450	/	21	8	14	21	12	19	13	8	6	6	1
50	40	450	20	450	11	4	1	2	3	4	8	9	5	6	4	5
10	10	450	50	450	/	64	2	26	6	12	9	8	/	5	31	31
50	10	450	50	450	/	4	1	5	5	2	3	/	/	9	35	8
10	40	450	50	450	/	/	18	/	52	29	19	/	/	/	/	26
50	40	450	50	450	/	16	1	12	2	7	4	/	/	/	/	6

Table S5: Variances in percentage of the performed measurements during the design of experiments for (+)APCI

A: sheath gas (AU)	B: auxiliary gas (AU)	C: capillary temperature (°C)	D: capillary voltage (V)	E: vaporizer temperature (°C)	Erythritol	1,3-cyclopentanedione	Catechol	2,5-hexanedione	Vanillyl alcohol	Guaiacol	Acetovanilone	Syringol	Acetophenone	4-ethylacetophenone	(3-phenoxyphenyl)methanol	Naphtoflavone
10	10	250	20	250	8	5	/	3	2	/	2	4	11	2	5	3
50	10	250	20	250	3	1	/	2	1	/	4	2	6	2	6	2
10	40	250	20	250	11	6	/	7	4	/	5	2	7	3	4	5
50	40	250	20	250	6	2	/	1	2	/	3	1	6	5	3	1
10	10	250	50	250	4	13	/	6	6	29	4	4	8	7	5	9
50	10	250	50	250	2	2	/	1	2	3	3	1	5	2	4	2
10	40	250	50	250	3	46	/	2	1	4	3	1	1	2	3	4
50	40	250	50	250	5	2	/	1	1	12	2	4	1	4	2	2
30	25	250	35	350	4	2	/	2	2	/	3	4	1	4	26	8
10	10	250	20	450	2	73	/	6	8	/	8	2	5	0	11	8
50	10	250	20	450	6	1	/	1	2	/	2	2	3	1	4	4
10	40	250	20	450	4	1	/	3	5	/	2	2	2	2	5	5
50	40	250	20	450	8	3	/	5	6	/	2	5	8	5	1	2
10	10	250	50	450	16	14	/	4	4	26	5	5	3	3	13	9
50	10	250	50	450	7	4	/	1	2	5	3	3	2	1	2	1
10	40	250	50	450	10	1	/	3	10	1	3	3	3	5	19	0
50	40	250	50	450	3	3	/	3	3	3	3	1	3	4	6	5
30	25	350	35	250	2	2	/	2	2	17	5	2	2	2	1	3
30	25	350	20	350	1	2	/	1	3	/	3	2	3	3	9	3
30	10	350	35	350	5	3	/	1	0	2	3	1	8	3	1	7
10	25	350	35	350	15	7	/	1	10	5	1	2	7	6	10	4
30	25	350	35	350	6	2	/	2	2	6	2	2	4	1	4	4
50	25	350	35	350	2	2	/	2	1	8	1	3	1	1	5	7
30	40	350	35	350	3	1	/	0	2	3	2	3	3	2	4	3
30	25	350	50	350	3	1	/	68	2	2	4	2	3	3	21	2
30	25	350	35	450	5	2	/	1	2	1	1	5	4	2	173	1
10	10	450	20	250	97	29	/	14	20	88	17	12	5	14	103	17

50	10	450	20	250	7	4	/	1	1	/	1	1	3	2	61	0
10	40	450	20	250	53	13	/	3	6	173	6	5	3	3	/	5
50	40	450	20	250	9	4	/	1	2	33	2	1	2	4	67	1
10	10	450	50	250	/	86	28	44	21	6	12	26	11	8	/	12
50	10	450	50	250	/	2	21	2	3	2	0	2	1	2	/	4
10	40	450	50	250	/	2	3	3	2	2	3	2	2	1	/	3
50	40	450	50	250	/	2	4	3	2	2	2	4	1	5	/	2
30	25	450	35	350	26	3	/	2	2	3	4	2	1	4	/	4
10	10	450	20	450	/	12	/	5	11	/	7	4	1	6	109	4
50	10	450	20	450	20	2	/	1	4	88	1	1	1	3	/	1
10	40	450	20	450	8	5	/	4	10	18	3	1	2	2	/	5
50	40	450	20	450	14	0	/	1	2	13	3	4	2	4	/	3
10	10	450	50	450	/	10	27	29	5	7	8	13	74	3	/	7
50	10	450	50	450	/	1	4	5	3	1	1	4	2	2	/	2
10	40	450	50	450	/	6	80	1	4	2	2	6	2	2	/	1
50	40	450	50	450	/	2	5	5	2	3	1	7	6	0	/	0

Figure S4: UV chromatogram at 254 nm (red) and BPC of negative ESI (blue) of a lignocellulosic biomass pyrolysis oil

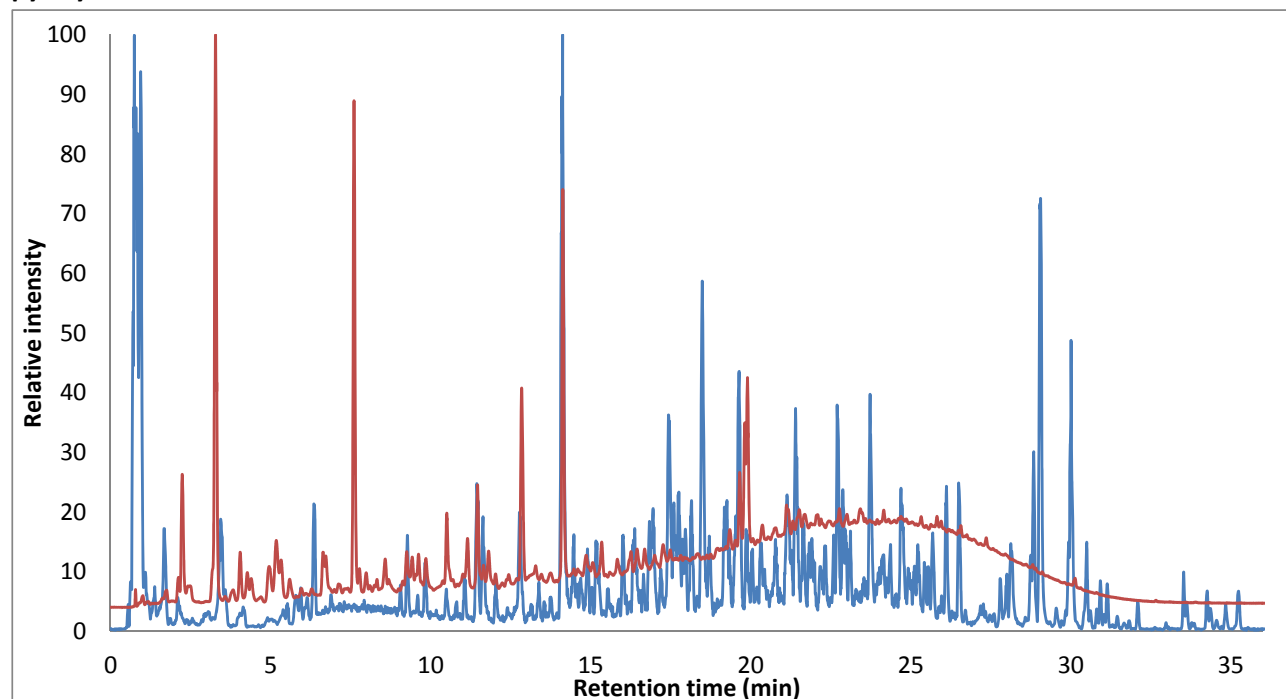


Figure S5: Comparison of heteroatom class distributions between LC(-)ESI/FT-ICR/MS and (-)ESI/FT-ICR/MS

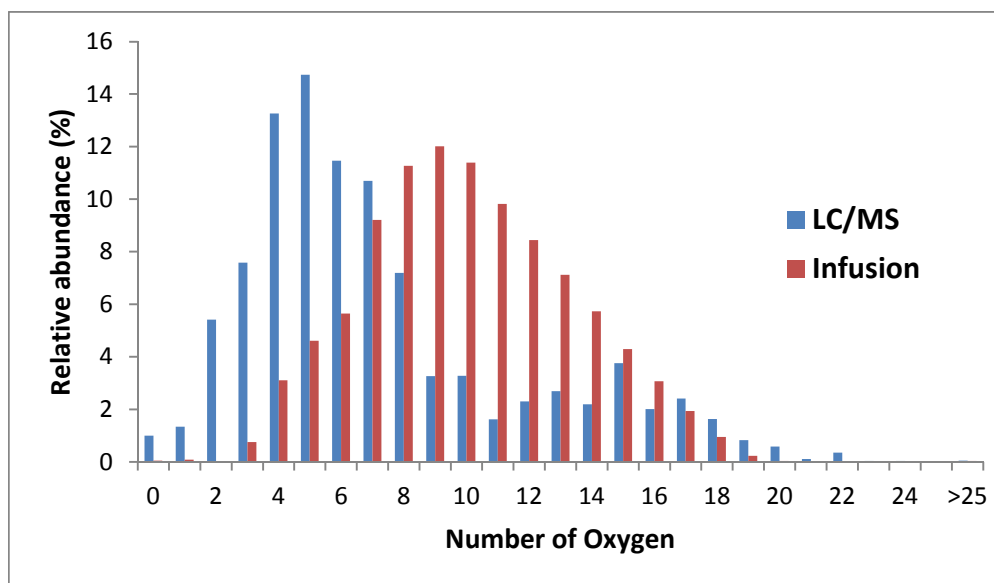


Figure S6 : Venn diagram representing the number of features detected for the four ionization modes (draw on http://bioinformatics.psb.ugent.be/cgi-bin/liste/Venn/calculate_venn.html)

