How are negative ions in an ICPMS formed? – electronic supplement

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Tables:

Figures:

Table S1: electronic and physical properties of atoms of interest (data taken from https://webbook.nist.gov/chemistry)

	F	Cl	Br	I	O
rel AMU	18.998493	35.45	79.904	126.90447	15.9994
Electronegativity (Pauling)	3.98	3.16	2.96	2.66	3.44
1. Ionisation energy (kJ/mol)	1681.05	1251.19	1139.86	1008.39	1313.94
Electron affinity (kJ/mol)	328	349	324.6	295.2	141
Electron affinity (eV)	3.401	3.612	3.363	3.059	1.44
Atomic size (pm)	50 (42)	100 (79)	115 (94)	140 (115)	60 (48)
Ionic radius (pm)	118	167	195	206	126
Pauli radius (pm)	136	181	195	216	140

Table S2: summary of instrumental detection limits from a selection of the literature for fluorine, chlorine and bromine

	Estimated l.o.d. (instrumental)	Lowest external std	untargeted	Literature used among others
fluorine				
ESI-MS/MS	from 0.05 to 5 µg compound / L	20 ng compound/L	no	Zhang *et al.*[1]
GC-MS / ECD	Low pg/m^3 sample	125 ng compound/L	(y)	Shoeib *et al.*[2], de Silva *et al.*[3]
CIC	<1 µg F/L to > 6 mg F /L	5.7 µg F/L[4] 50 mg/L[5]	-	Koch *et al.*[6] Spaan *et al.*[5]
HR-CS-MAS	10 -160 µg F/L		-	Gleisner *et al.*[7,8], Ley *et al.*[7,8]
ICPMS/MS	21 (total) 500 µg F/L (speciation)	0.1 mg F/L[9] 0.25 mg F/L[10] 0.5 mg F/L[11] 0.06 mg F/L	(y)	Guo *et al.*[9,11], Jamari *et al.*[10] Zhu *et al.*[12]
HR-ICPMS	5 mg/L	200 mg F/L	-	Bu *et al.*[13]
PARCI	20 µg F /L 7.6 – 21 µg/L[14]		y	Redeker *et al.*[14]
chlorine				
ESI-MS/MS	4-88 µg compound/kg in sample[5]		y	Spaan *et al.*[5]
GC-MS / ECD	Low pg-range (on-column) 2.3 ng/g (sample)[15]	1 µg compound/L[16]	y	Xu *et al.*[17]
CIC	<0.9 µg Cl/L[18] 340 µg Cl/L[5]	11 µg Cl/L[4] 75 µg Cl/L[5]	-	Spaan *et al.*[5]
HR-CS-MAS	9.6 µg Cl/L[19]	10 µg Cl/L[19]	-	Abad *et al.*[19]
ICPMS/MS	0.3 µg - 5 Cl/L[20,21] 1 µg/L[22] <5 µg Cl/L[21]	10 µg/L[20]	(y)	Lajin *et al.* [20, 21] Klencsar *et al.*[22]
HR-ICPMS	3 µg/L[13]	50 µg Cl/L	-	Bu *et al.*[13,23]
PARCI	7 µg Cl/L[14,24] 25-57 µg/L[14]	~200 µg/L[14]	y	Redeker *et al.*[14] Lesniewski *et*

				al.[24]
bromine				
APPI-MS/MS	< 30 pg (on-column) ESI ~ 0-0.5 µg/kg sample[5]	35 µg compound/L[253]	no	Lagalante *et al.*[23]
GC-MS	0.04 – 85 pg (on-column)		y	Xu *et al.*[17]
CIC	2.7 – 7.1 µg/L[18] < 250 µg/L[5]	250 µg/L[5]	-	Spaan *et al.*[5]
HR-CS-MAS	160 µg/L[26]		-	Gunduz *et al.*[24]
ICPMS/MS	0.4 µg Br/L[22] 0.8[20] -15 µg Br/L[21]	10 µg Br/L[20]	y	Lajin *et al.*[20,21] Klencsar *et al.*[22]
HR-ICPMS	0.08 µg/L	5 µg/L	-	Bu *et al.*[13,23]

Influence of sampling depth on signal intensity and OH-contribution

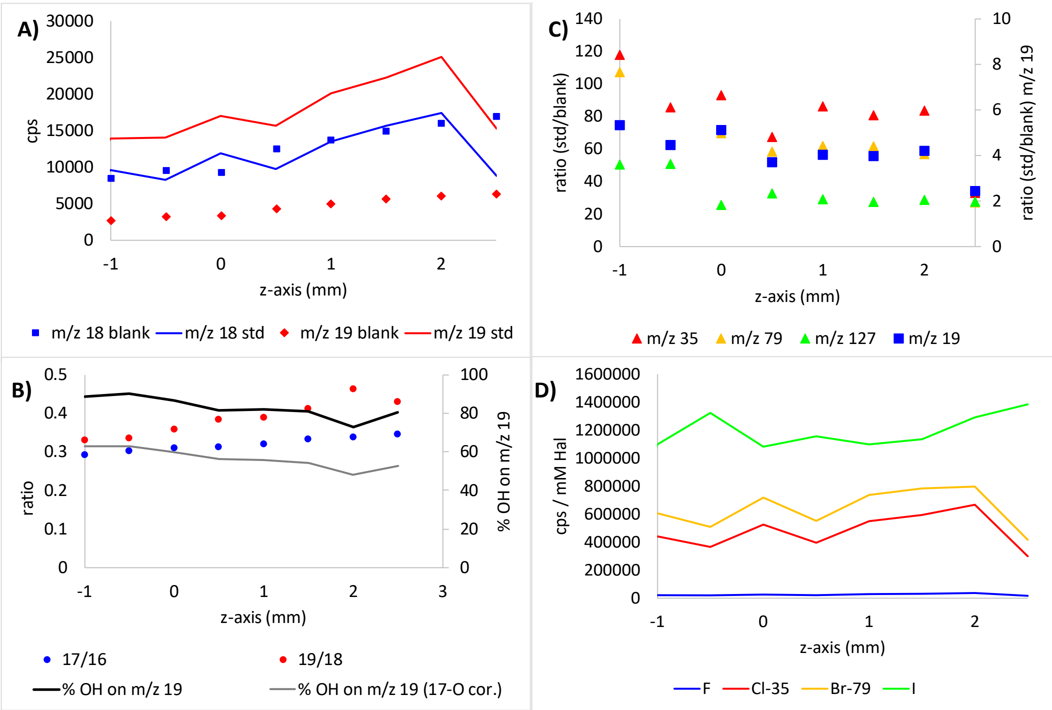

Figure S1: influence of sampling depth on intensity; A) intensities of m/z 18 and 19 in blank and 10 mg Hal/L standard solution; B) ratios of 17/16 and 19/18 at reduced detector voltage and calculated minimum and maximum OH^- contribution to m/z 19 in blank solution; C) standard/blank ratios; D) signal intensity (in cps/mM Hal); all other instrument settings were static (see Table 1)

Influence of auxiliary gas settings on signal intensity and OH-contribution

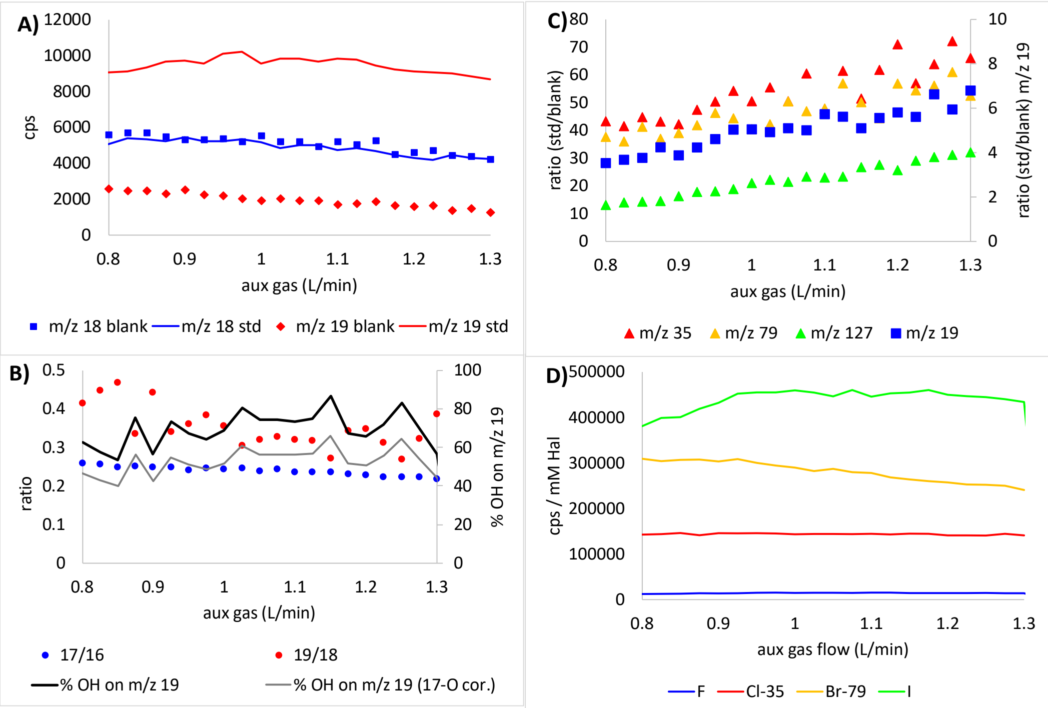

Figure S2: influence of auxiliary gas flow on intensity; A) intensities of m/z 18 and 19 in blank and 10 mg Hal/L standard solution; B) ratios of 17/16 and 19/18 at reduced detector voltage and calculated minimum and maximum OH^- contribution to m/z 19 in blank solution; C) standard/blank ratios; D) signal intensity (in cps/mM Hal); all other instrument settings were static (see Table 1)

Influence of cell entrance/exit lens settings on signal intensity and OH-contribution

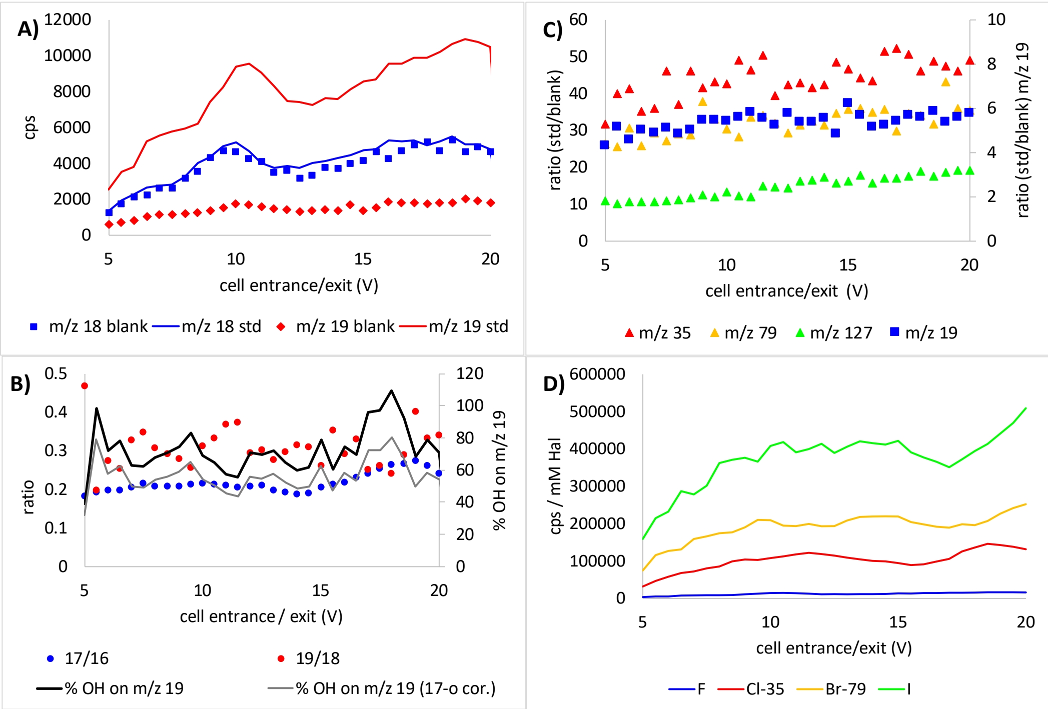

Figure S3: influence of cell entrance/exit voltage on intensity; A) intensities of m/z 18 and 19 in blank and 10 mg Hal/L standard solution; B) ratios of 17/16 and 19/18 at reduced detector voltage and calculated minimum and maximum OH^- contribution to m/z 19 in blank solution; C) standard/blank ratios; D) signal intensity (in cps/mM Hal); all other instrument settings were static (see Table 1)

Influence of cell rod offset settings on signal intensity and OH-contribution

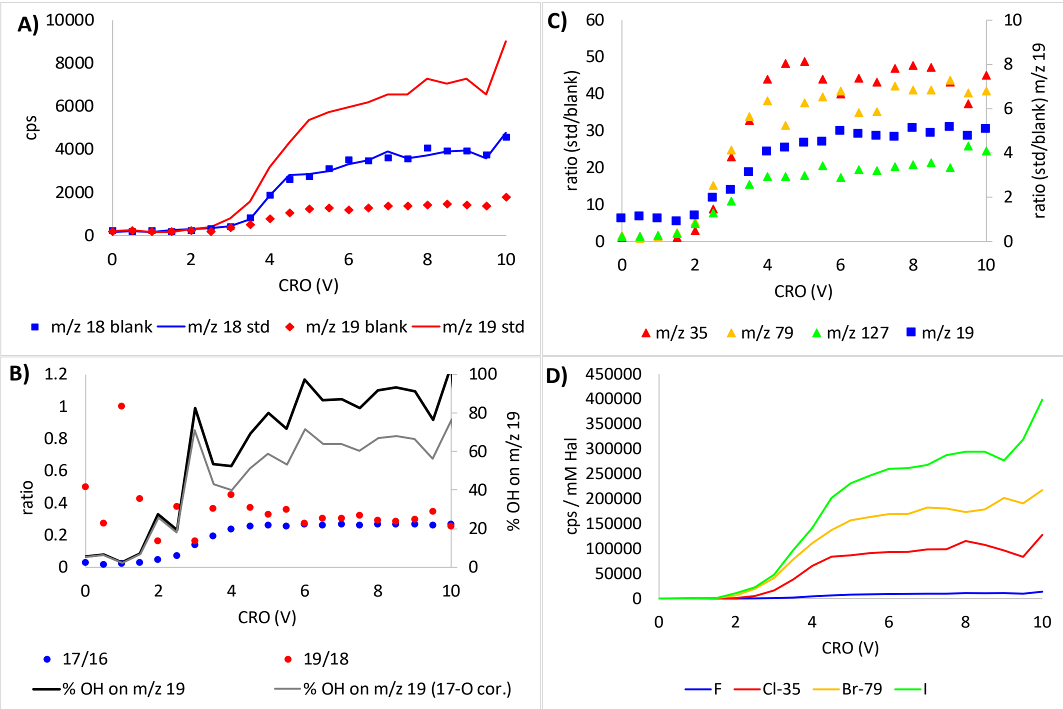

Figure S4: influence of cell rod offset voltage on intensity; A) intensities of m/z 18 and 19 in blank and 10 mg Hal/L standard solution; B) ratios of 17/16 and 19/18 at reduced detector voltage and calculated minimum and maximum OH^- contribution to m/z 19 in blank solution; C) standard/blank ratios; D) signal intensity (in cps/mM Hal); all other instrument settings were static (see Table 1)

Influence of quadrupole rod offset settings on signal intensity and OH-contribution

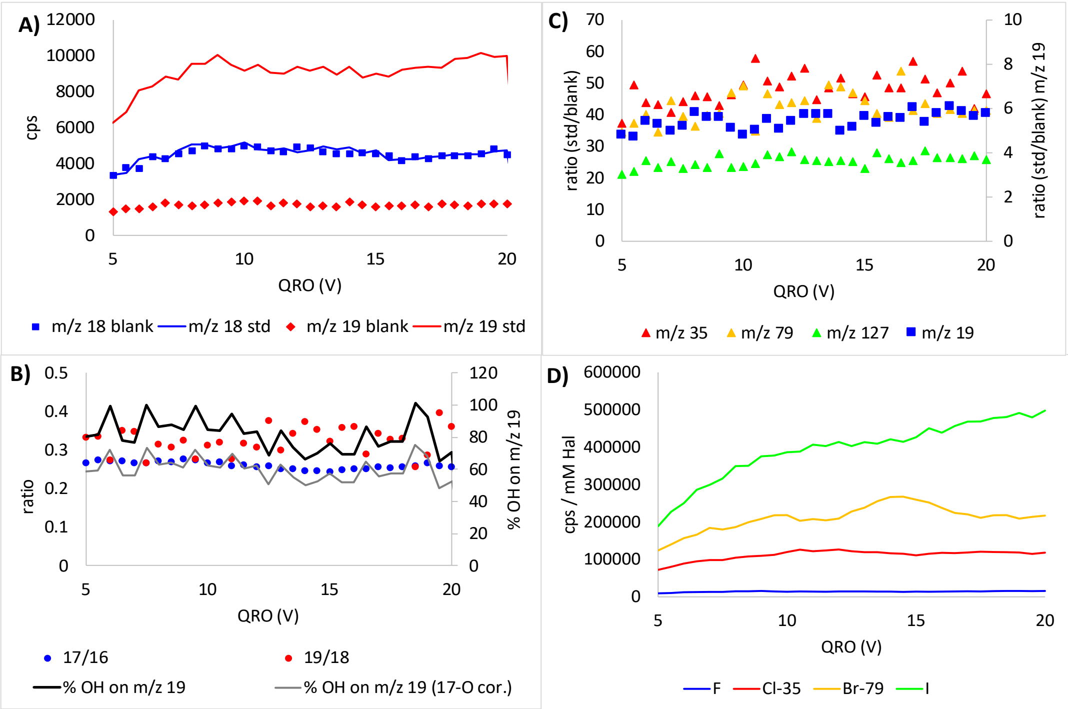

Figure S5: influence of quadrupole rod offset voltage on intensity; A) intensities of m/z 18 and 19 in blank and 10 mg Hal/L standard solution; B) ratios of 17/16 and 19/18 at reduced detector voltage and calculated minimum and maximum OH^- contribution to m/z 19 in blank solution; C) standard/blank ratios; D) signal intensity (in cps/mM Hal); all other instrument settings were static (see Table 1)

Influence of QID voltage settings on signal intensity and OH-contribution

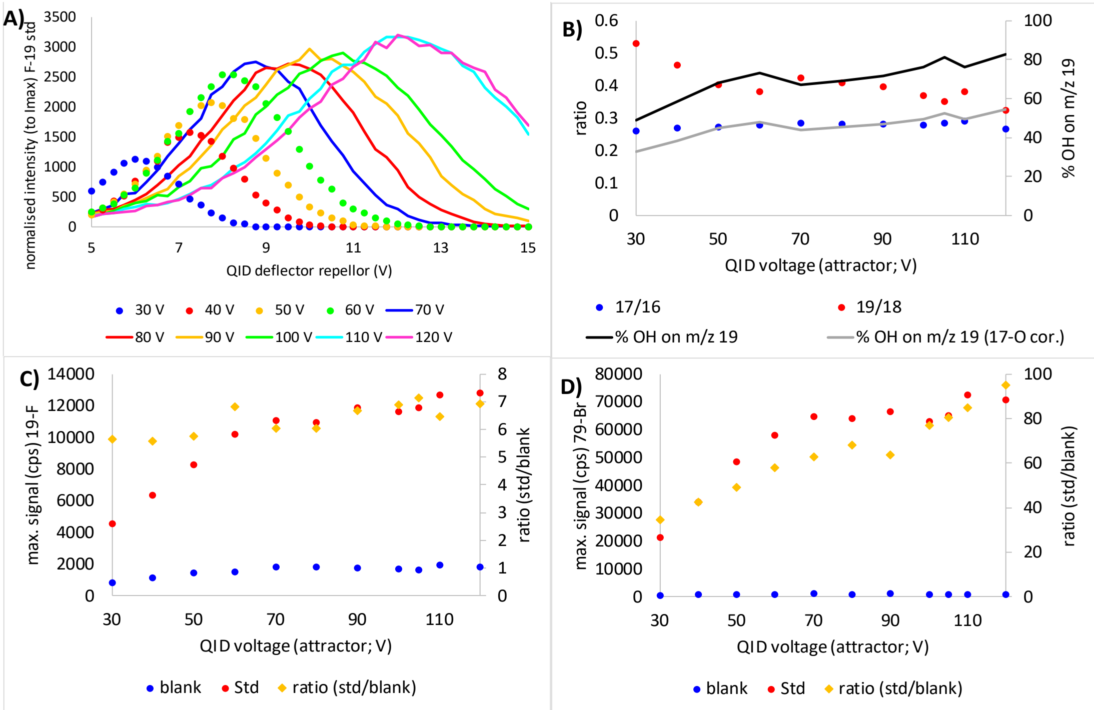

Figure S6: A) intensity at various QID attractor, box and entrance voltage settings (ratio attractor: box 1: 0.66, attractor: entrance 1: 0.37) versus QID deflector repellor voltage; B) ratio 17/16 and 19/18 and calculated % OH contribution at signal maximum at the indicated QID attractor voltage; C) intensity and standard / blank ratio at signal maximum for m/z 19; D) intensity and standard / blank ratio at signal maximum for m/z 79

Influence of QID attractor voltage settings on signal intensity and OH- contribution

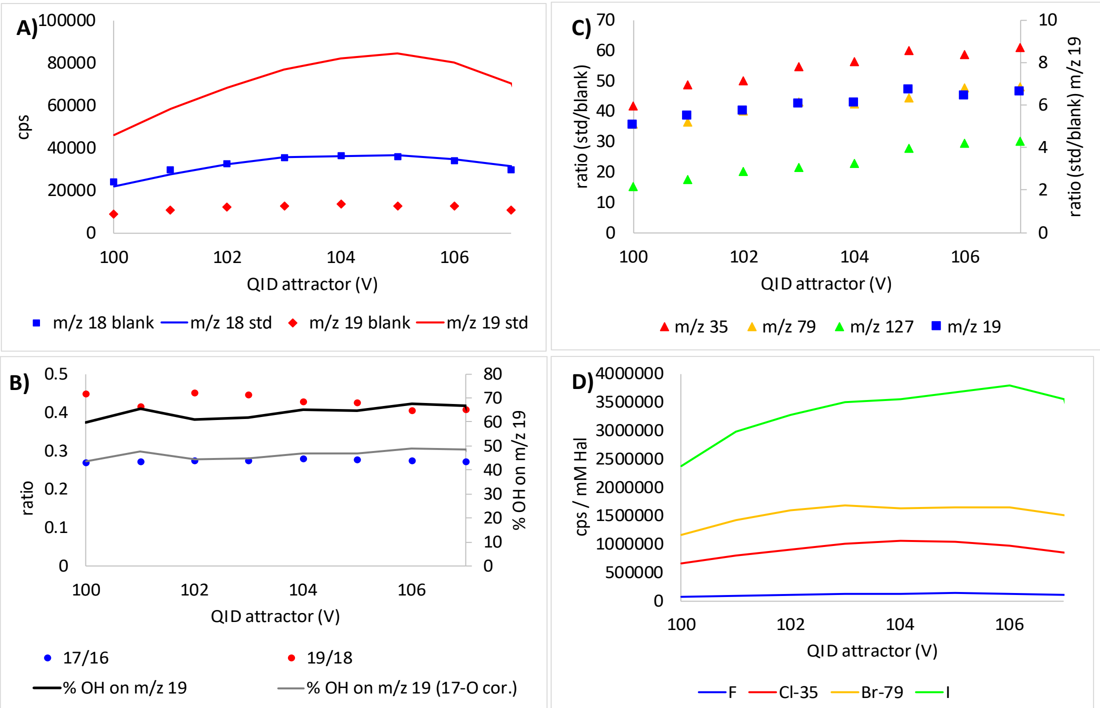

Figure S7: influence of QID attractor voltage on intensity; A) intensities of m/z 18 and 19 in blank and 10 mg Hal/L standard solution; B) ratios of 17/16 and 19/18 at reduced detector voltage and calculated minimum and maximum OH^- contribution to m/z 19 in blank solution; C) standard/blank ratios; D) signal intensity (in cps/mM Hal); all other instrument settings were static (see Table 1)

Influence of QID box voltage settings on signal intensity and OH-contribution

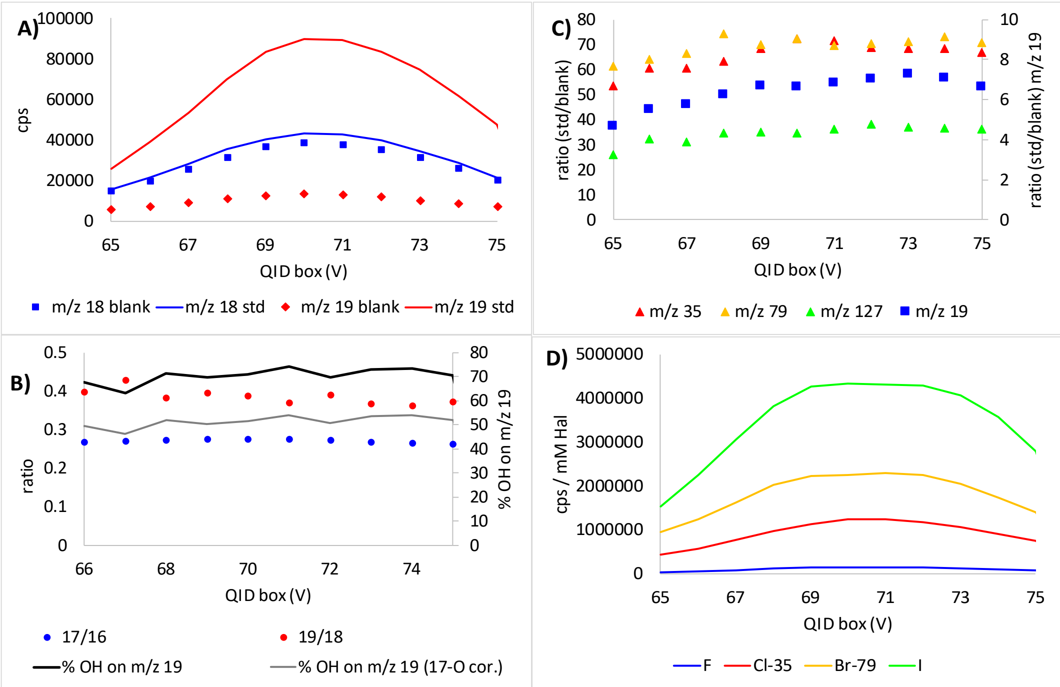

Figure S8: influence of QID box voltage on intensity; A) intensities of m/z 18 and 19 in blank and 10 mg Hal/L standard solution; B) ratios of 17/16 and 19/18 at reduced detector voltage and calculated minimum and maximum OH^- contribution to m/z 19 in blank solution; C) standard/blank ratios; D) signal intensity (in cps/mM Hal); all other instrument settings were static (see Table 1)

Influence of QID entrance voltage settings on signal intensity and OH- contribution

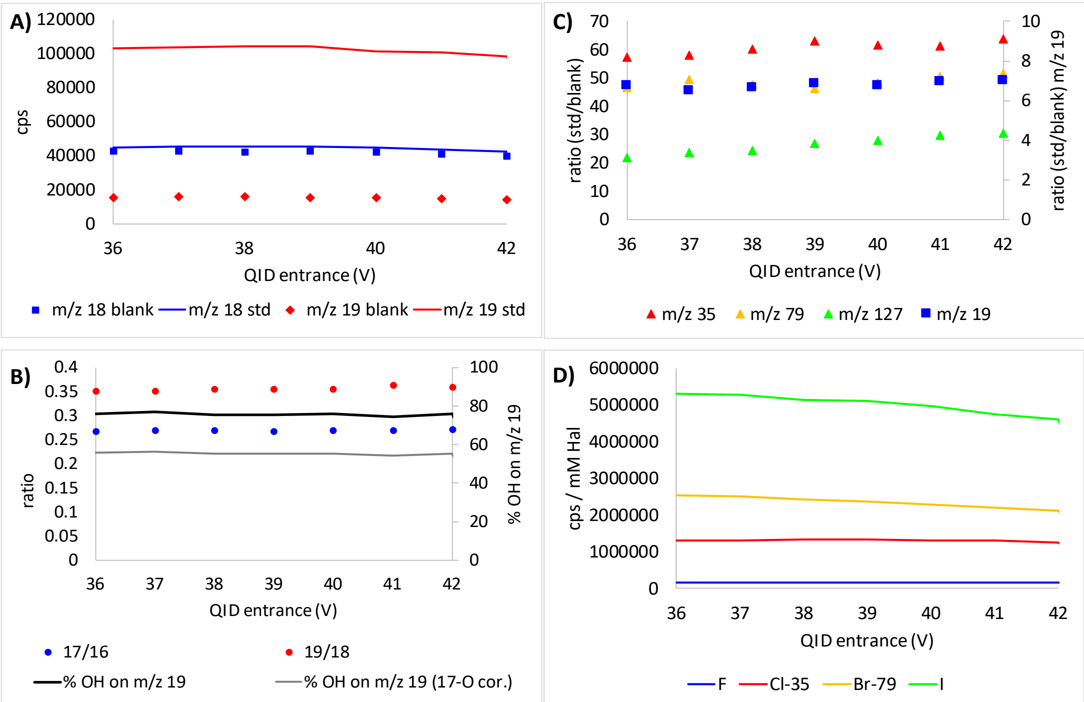

Figure S9: influence of QID entrance voltage on intensity; A) intensities of m/z 18 and 19 in blank and 10 mg Hal/L standard solution; B) ratios of 17/16 and 19/18 at reduced detector voltage and calculated minimum and maximum OH^- contribution to m/z 19 in blank solution; C) standard/blank ratios; D) signal intensity (in cps/mM Hal); all other instrument settings were static (see Table 1)

Influence of QID deflector repellor voltage settings on signal intensity and OH-contribution

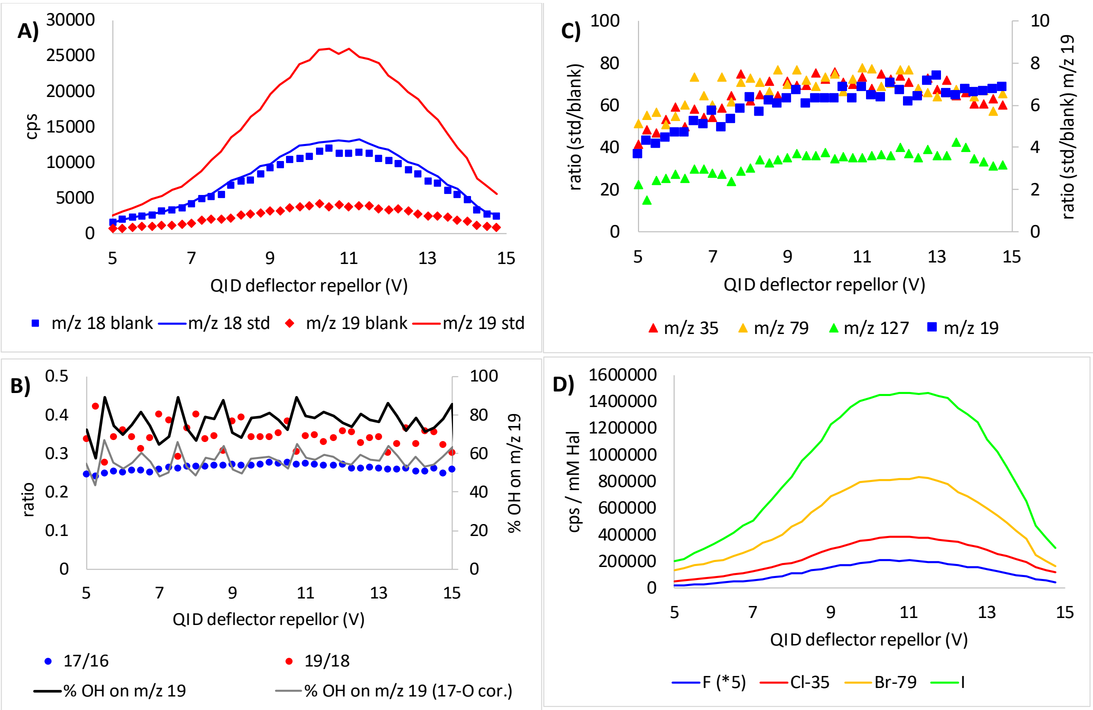

Figure S10: influence of QID deflector repellor voltage on intensity; A) intensities of m/z 18 and 19 in blank and 10 mg Hal/L standard solution; B) ratios of 17/16 and 19/18 at reduced detector voltage and calculated minimum and maximum OH^- contribution to m/z 19 in blank solution; C) standard/blank ratios; D) signal intensity (in cps/mM Hal); all other instrument settings were static (see Table 1)

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