

Electronic Supplementary Information

Elemental Detection of Fluorochemicals by Nanospray-Induced Chemical Ionization in Afterglow of an Inductively Coupled Plasma

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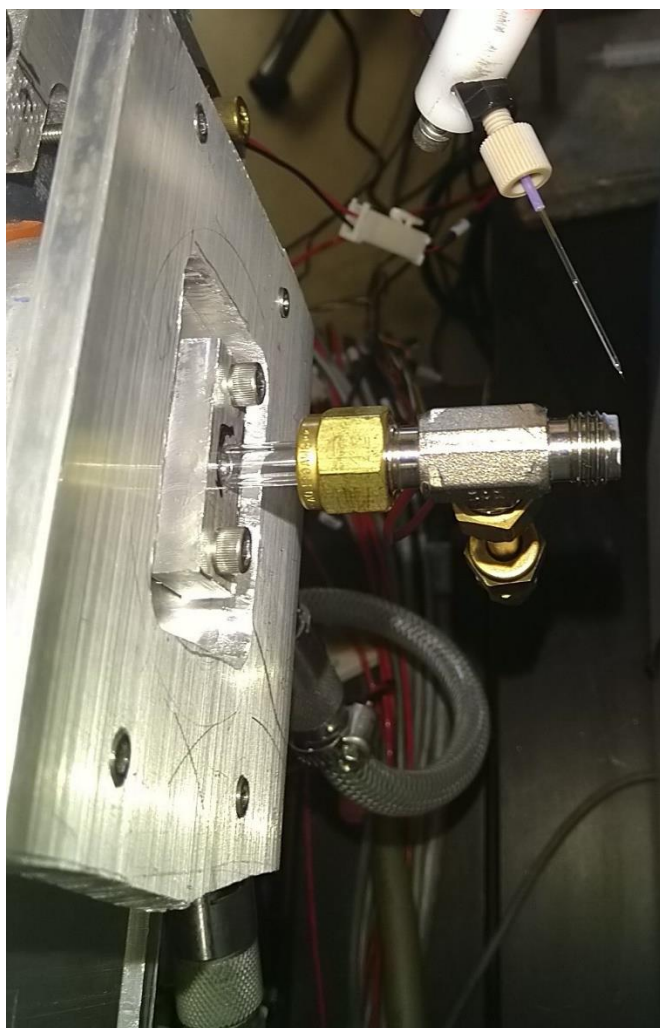


Figure S1. Ionization area of the ICP-nanospray-MS setup, showing the cooled aluminum plate of the ICP interface coupled to a quartz plasma sampling tube, a venturi tee, and a nanospray emitter.

Examination of soft ion sampling spectrum. To investigate the effect of fragmentation during ion sampling on appearance of BaOH^+ and m/z 168, we collected a background spectrum with softer sampling by lowering declustering potential (DP) from 50 V to 10 V. Figure S2 provides annotation of ions with intensities ≥ 320000 cps. This intensity threshold was established based on the lowest intensity hydrated barium species detected in the spectra, namely $\text{BaOH}(\text{H}_2\text{O})^+$, and corresponds to 4.4% of that of the most intense ion in the spectrum, providing a reasonable cut off threshold for identification of potential reagent ions. A list of ions and their intensities is tabulated in Table S1.

As noted in Figure S2 and Table S1, several solvated species of each core ion are detected. The solvation is dramatically reduced via ion activation at declustering potential of 50 V (see Figure 7A in the article). Therefore, to compare the prevalence of core ions between declustering potentials of 50 and 10 V, we utilized an aggregate intensity equal to the sum of intensities of each core ion and its solvated species. For example, for the core ion BaOH^+ three solvated ions have been detected in soft sampling conditions, BaOH^+ , $\text{BaOH}(\text{H}_2\text{O})^+$, and $\text{BaOH}(\text{H}_2\text{O})_2^+$, with intensities of 596124, 664138, and 492102 cps, respectively, resulting in total prevalence of 1752364 for this core ion.

Table S2 summarizes such aggregate intensities for each core ion at both soft (10 V DP) and harsh (50 V DP) ion sampling conditions. The ratio of the intensities between the two sampling conditions provides a metric for the effect of ion sampling on prevalence of each core ion. Notably, only BaOH^+ and m/z 168 show a significant improvement in prevalence when harsh ion sampling is utilized, supporting the hypothesis that these species are mainly products of fragmentation in ion sampling.

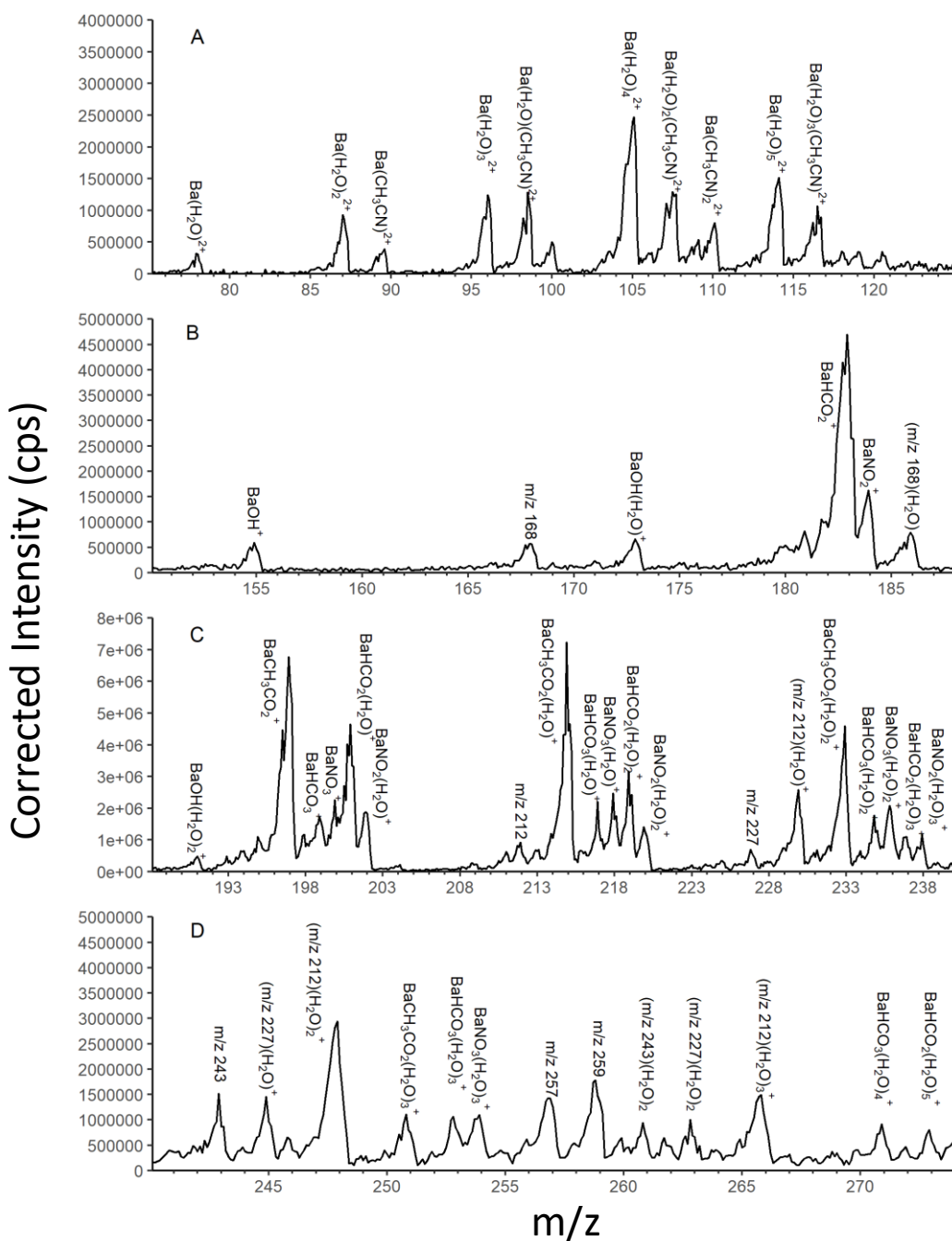


Figure S2. Proposed ion formulas in background spectrum of ICP-nanospray-MS using soft ion sampling conditions (declustering potential of 10 V) and 1 mM barium acetate as the nanospray electrolyte. Note that the total spectrum is split to four m/z ranges via panels A to D for ease of presentation. A sampling orifice size of 4 mm and a N_2 gas flow rate of 2.1 L/min introduced into the venturi tee were utilized in these experiments.

Table S1. Ion intensities using soft ion sampling conditions

m/z	Ion	Intensity (cps)	m/z	Ion	Intensity (cps)
78	Ba(H ₂ O) ⁺²	320067	217	BaHCO ₃ (H ₂ O) ⁺	2208460
87	Ba(H ₂ O) ₂ ⁺²	928193	218	BaNO ₃ (H ₂ O) ⁺	2472515
89.5	Ba(CH ₃ CN) ⁺²	388081	219	BaHCO ₂ (H ₂ O) ₂ ⁺	3164659
96	Ba(H ₂ O) ₃ ⁺²	1244259	220	BaNO ₂ (H ₂ O) ₂ ⁺	1408293
98.5	Ba(H ₂ O)(CH ₃ CN) ⁺²	1284267	227	Unknown	692144
105	Ba(H ₂ O) ₄ ⁺²	2472515	230	(m/z 212)(H ₂ O)	2584538
107.5	Ba(H ₂ O) ₂ (CH ₃ CN) ⁺²	1288268	233	BaCH ₃ CO ₂ (H ₂ O) ₂ ⁺	4592956
110	Ba(CH ₃ CN) ₂ ⁺²	804167	235	BaHCO ₃ (H ₂ O) ₂ ⁺	1768368
114	Ba(H ₂ O) ₅ ⁺²	1516316	236	BaNO ₃ (H ₂ O) ₂ ⁺	2080433
116.5	Ba(H ₂ O) ₃ (CH ₃ CN) ⁺²	1068222	237	BaHCO ₂ (H ₂ O) ₃ ⁺	1096228
155	BaOH ⁺	596124	238	BaNO ₂ (H ₂ O) ₃ ⁺	1172244
168	Unknown	564117	243	Unknown	1516315
173	BaOH(H ₂ O) ⁺	664138	245	(m/z 245)(H ₂ O)	1456303
183	BaHCO ₂ ⁺	4700979	248	(m/z 212)(H ₂ O) ₂	2944613
184	BaNO ₂ ⁺	1624338	251	BaCH ₃ CO ₂ (H ₂ O) ₃ ⁺	1104230
186	(m/z 168)(H ₂ O)	796166	253	BaHCO ₃ (H ₂ O) ₃ ⁺	1068222
191	BaOH(H ₂ O) ₂ ⁺	492102	254	BaNO ₃ (H ₂ O) ₃ ⁺	1100229
197	BaCH ₃ CO ₂ ⁺	6773410	257	Unknown	1432298
199	BaHCO ₃ ⁺	1736362	259	Unknown	1784372
200	BaNO ₃ ⁺	2260471	261	(m/z 243)(H ₂ O)	944190
201	BaHCO ₂ (H ₂ O) ⁺	4648968	263	(m/z 227)(H ₂ O) ₂	1004205
202	BaNO ₂ (H ₂ O) ⁺	1888393	266	(m/z 212)(H ₂ O) ₃	1492311
212	Unknown	924192	271	BaCH ₃ CO ₂ (H ₂ O) ₄ ⁺	912190
215	BaCH ₃ CO ₂ (H ₂ O) ⁺	7233506			

Table S2. Core ion aggregate intensities

Core Ion	Aggregate Intensity in Soft Sampling (cps)	Aggregate Intensity in Harsh Sampling (cps)	Ratio of Harsh to Soft Sampling Intensities
Ba ²⁺	11314355	6141850	0.5
BaOH ⁺	1752364	3965969	2.3
m/z 168	1360283	6033828	4.4
BaHCO ₂ ⁺	13610834	15730133	1.2
BaNO ₂ ⁺	6093268	6116130	1.0
BaCH ₃ CO ₂ ⁺	19704102	20035601	1.0
BaHCO ₃ ⁺	7693602	3112077	0.4
BaNO ₃ ⁺	7913648	5352257	0.7
m/z 212	7945654	779305	0.1
m/z 227	3152652	936194	0.3
m/z 243	2460505	938767	0.4
m/z 257	1432298	Not Detected	N/A
m/z 259	1784372	1085369	0.6

The ions with assigned formulas account for 79% and 86% of the total major ion intensities in soft and harsh ion sampling conditions, respectively.

Optimized geometries and energies (Hartree/particle) at ω B97xD/aug-cc-pVTZ level of theory:

BaCH₃CO₂⁺

Element Coordinates (Angstroms)
 X Y Z

Ba	-1.054308	-0.000016	0.001278
O	1.126496	1.100688	-0.006516
O	1.126475	-1.100497	-0.006600
C	1.766922	0.000106	-0.012420
C	3.257698	-0.000044	0.001390
H	3.643663	0.899460	-0.469062
H	3.643281	-0.896650	-0.474952
H	3.582826	-0.003820	1.043543

Rotational symmetry number = 1
Zero-point correction= 0.050552
Sum of electronic and zero-point Energies= -253.834195
Sum of electronic and thermal Energies= -253.828013
Sum of electronic and thermal Enthalpies= -253.827069
Sum of electronic and thermal Free Energies= -253.867057

BaF⁺

Element	Coordinates (Angstroms)		
	X	Y	Z
F	0.000000	0.000000	-1.824729
Ba	0.000000	0.000000	0.293260

Rotational symmetry=	1
Zero-point correction=	0.001198
Sum of electronic and zero-point Energies=	-125.224971
Sum of electronic and thermal Energies=	-125.222405
Sum of electronic and thermal Enthalpies=	-125.221460
Sum of electronic and thermal Free Energies=	-125.248642

BaF(H₂O)₂⁺

Element	Coordinates (Angstroms)		
	X	Y	Z
Ba	-0.000000	-0.564054	0.065697
O	-2.200676	0.797206	-0.563469
H	-1.945093	1.620238	-0.125336
H	-3.062469	0.930024	-0.960414
O	2.200676	0.797204	-0.563470
H	1.945094	1.620236	-0.125335
H	3.062470	0.930022	-0.960417
F	0.000002	1.525694	0.834223

Rotational symmetry=	1
Zero-point correction=	0.051000
Sum of electronic and zero-point Energies=	-278.132649
Sum of electronic and thermal Energies=	-278.124440
Sum of electronic and thermal Enthalpies=	-278.123496
Sum of electronic and thermal Free Energies=	-278.166896

Ba(H₂O)₃⁺²

Element	Coordinates (Angstroms)		
	X	Y	Z
Ba	0.000245	-0.000525	-0.279599
O	-2.313402	-1.090543	0.488586
H	-2.446557	-1.808923	1.117603
H	-3.202606	-0.865705	0.191335
O	2.102391	-1.454420	0.489265
H	2.797934	-1.203314	1.107646
H	2.347402	-2.341462	0.201886
O	0.209930	2.547533	0.488683
H	0.842072	3.209108	0.184893
H	-0.343328	3.019131	1.121898

Rotational symmetry=	3
Zero-point correction=	0.072644
Sum of electronic and zero-point Energies=	-254.321555
Sum of electronic and thermal Energies=	-254.310582
Sum of electronic and thermal Enthalpies=	-254.309638
Sum of electronic and thermal Free Energies=	-254.363051

BaHCO₂⁺

Element	Coordinates (Angstroms)		
	X	Y	Z
Ba	-0.711409	0.000000	-0.000000
O	1.497801	-1.104647	0.000000
O	1.497802	1.104647	0.000000
C	2.111233	-0.000000	-0.000000
H	3.206701	-0.000001	-0.000002

Rotational symmetry number=	2
Zero-point correction=	0.023022
Sum of electronic and zero-point Energies=	-214.529073
Sum of electronic and thermal Energies=	-214.524665
Sum of electronic and thermal Enthalpies=	-214.523721
Sum of electronic and thermal Free Energies=	-214.557767

BaHCO₃⁺

Element	Coordinates (Angstroms)		
	X	Y	Z
Ba	-1.025791	-0.005978	-0.000001
O	1.188757	-1.095252	0.000004
O	1.135406	1.119154	0.000004
C	1.779407	0.031705	0.000002
O	3.090601	0.094193	-0.000005
H	3.449761	-0.800191	-0.000001

Rotational symmetry number= 1
Zero-point correction= 0.028834
Sum of electronic and zero-point Energies= -289.785049
Sum of electronic and thermal Energies= -289.779940
Sum of electronic and thermal Enthalpies= -289.778996
Sum of electronic and thermal Free Energies= -289.815845

BaNO₂⁺

Element	Coordinates (Angstroms)		
	X	Y	Z
Ba	0.723789	-0.000000	-0.000096
N	-2.243898	0.000002	0.000358
O	-1.551552	1.051823	0.000181
O	-1.551559	-1.051822	0.000180

Rotational symmetry number= 2
Zero-point correction= 0.009342
Sum of electronic and zero-point Energies= -230.465677
Sum of electronic and thermal Energies= -230.461078
Sum of electronic and thermal Enthalpies= -230.460133
Sum of electronic and thermal Free Energies= -230.494952

BaNO₃⁺

Element	Coordinates (Angstroms)		
	X	Y	Z
N	0.000000	-1.906549	0.000000
O	-1.083483	-1.207823	0.000000
O	1.083481	-1.207823	0.000000
O	0.000000	-3.084568	0.000000
Ba	0.000000	1.024063	0.000000

Rotational symmetry number=	2
Zero-point correction=	0.015811
Sum of electronic and zero-point Energies=	-305.667645
Sum of electronic and thermal Energies=	-305.662794
Sum of electronic and thermal Enthalpies=	-305.661850
Sum of electronic and thermal Free Energies=	-305.697638

BaOH⁺

Element	Coordinates (Angstroms)		
	X	Y	Z
Ba	0.003773	-0.309671	-0.000000
O	0.003773	1.824496	0.000000
H	-0.241442	2.745579	0.000000

Rotational symmetry number=	1
Zero-point correction=	0.011228
Sum of electronic and zero-point Energies=	-101.175270
Sum of electronic and thermal Energies=	-101.171925
Sum of electronic and thermal Enthalpies=	-101.170981
Sum of electronic and thermal Free Energies=	-101.199396

CO₂

Element	Coordinates (Angstroms)		
	X	Y	Z
C	0.000000	0.000000	0.000000
O	0.000000	0.000000	1.156497
O	0.000000	0.000000	-1.156497

Rotational symmetry number= 2
Zero-point correction= 0.011877
Sum of electronic and zero-point Energies= -188.586595
Sum of electronic and thermal Energies= -188.583991
Sum of electronic and thermal Enthalpies= -188.583047
Sum of electronic and thermal Free Energies= -188.607276

H₂CO₃

Element	Coordinates (Angstroms)		
	X	Y	Z
O	-1.083284	-0.675457	-0.000020
O	0.000007	1.298796	-0.000093
C	-0.000000	0.098509	-0.000007
O	1.083278	-0.675465	0.000116
H	1.843697	-0.087028	0.000121
H	-1.843698	-0.087013	-0.000108

Rotational symmetry number=	2
Zero-point correction=	0.040335
Sum of electronic and zero-point Energies=	-264.995631
Sum of electronic and thermal Energies=	-264.991960
Sum of electronic and thermal Enthalpies=	-264.991015
Sum of electronic and thermal Free Energies=	-265.020835

H₂O

Element	Coordinates (Angstroms)		
	X	Y	Z
O	0.000000	0.000000	0.116444
H	0.000000	0.760003	-0.465774
H	-0.000000	-0.760003	-0.465774

Rotational symmetry number= 2
Zero-point correction= 0.021646
Sum of electronic and zero-point Energies= -76.418282
Sum of electronic and thermal Energies= -76.415447
Sum of electronic and thermal Enthalpies= -76.414502
Sum of electronic and thermal Free Energies= -76.435910

H₃O⁺

Element	Coordinates (Angstroms)		
	X	Y	Z
O	0.000000	0.000000	0.073417
H	0.000000	0.936910	-0.195779
H	0.811388	-0.468455	-0.195779
H	-0.811388	-0.468455	-0.195779

Rotational symmetry number=	3
Zero-point correction=	0.034879
Sum of electronic and zero-point Energies=	-76.682618
Sum of electronic and thermal Energies=	-76.679713
Sum of electronic and thermal Enthalpies=	-76.678768
Sum of electronic and thermal Free Energies=	-76.700703

CH₃CO₂H

Element	Coordinates (Angstroms)		
	X	Y	Z
C	0.000000	0.153620	0.000000
C	1.052240	-0.914069	0.000000
O	0.197069	1.337514	0.000000
H	2.035505	-0.456382	0.000000
H	0.932535	-1.547175	0.878222
H	0.932535	-1.547175	-0.878222
O	-1.241602	-0.369775	0.000000
H	-1.857748	0.371517	0.000000

Rotational symmetry number=	1
Zero-point correction=	0.062255
Sum of electronic and zero-point Energies=	-229.045439
Sum of electronic and thermal Energies=	-229.040873
Sum of electronic and thermal Enthalpies=	-229.039929
Sum of electronic and thermal Free Energies=	-229.072735

HF

Element	Coordinates (Angstroms)		
	X	Y	Z
H	0.000000	0.000000	-0.826602
F	0.000000	0.000000	0.091845

Rotational symmetry number=	1
Zero-point correction=	0.009458
Sum of electronic and zero-point Energies=	-100.451878
Sum of electronic and thermal Energies=	-100.449518
Sum of electronic and thermal Enthalpies=	-100.448574
Sum of electronic and thermal Free Energies=	-100.468277

HNO₂

Element	Coordinates (Angstroms)		
	X	Y	Z
O	-1.092843	-0.219826	-0.000001
N	-0.165955	0.481674	0.000001
H	1.705046	0.427828	-0.000006
O	1.024923	-0.255117	0.000001

Rotational symmetry number=	1
Zero-point correction=	0.020791
Sum of electronic and zero-point Energies=	-205.699832
Sum of electronic and thermal Energies=	-205.696644
Sum of electronic and thermal Enthalpies=	-205.695700
Sum of electronic and thermal Free Energies=	-205.723778

HNO₃

Element	Coordinates (Angstroms)		
	X	Y	Z
N	-0.143366	0.034666	0.000000
O	1.112081	-0.554669	-0.000000
O	-0.156239	1.237185	-0.000000
O	-1.044557	-0.738184	-0.000000
H	1.713288	0.202682	0.000000

Rotational symmetry number=	1
Zero-point correction=	0.027109
Sum of electronic and zero-point Energies=	-280.886260
Sum of electronic and thermal Energies=	-280.882797
Sum of electronic and thermal Enthalpies=	-280.881852
Sum of electronic and thermal Free Energies=	-280.911948

HCO₂H

Element	Coordinates (Angstroms)		
	X	Y	Z
C	0.133491	0.397580	0.000004
O	1.128396	-0.263469	0.000005
O	-1.110898	-0.089707	-0.000007
H	0.106733	1.493071	0.000016
H	-1.047668	-1.053142	-0.000016

Rotational symmetry number=	1
Zero-point correction=	0.034175
Sum of electronic and zero-point Energies=	-189.745763
Sum of electronic and thermal Energies=	-189.742603
Sum of electronic and thermal Enthalpies=	-189.741659
Sum of electronic and thermal Free Energies=	-189.769825