Supplementary Information for

Enhanced detection of aromatic oxidation products using NO_3^- chemical ionization mass spectrometry with limited nitric acid

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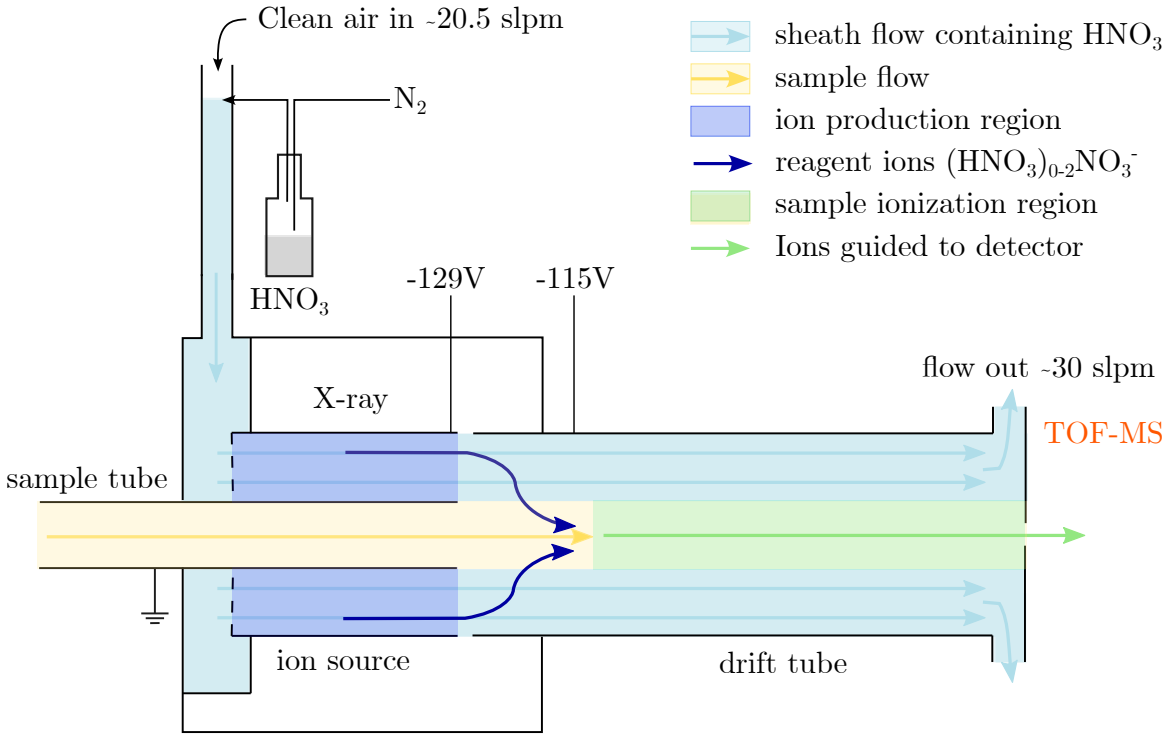

Figure S1. The schematic of Eisele-type nitrate ion chemical ionization inlet. Indicated values for flows and voltages correspond to the ones used in this study. Two regions where HNO_3 concentration can affect instrumental sensitivity are the ion production region and the sample ionization region. The flows in this schematic are approximated as ideal. In real conditions, some diffusion of neutral HNO_3 from the sheath flow into the sample ionization region may happen.

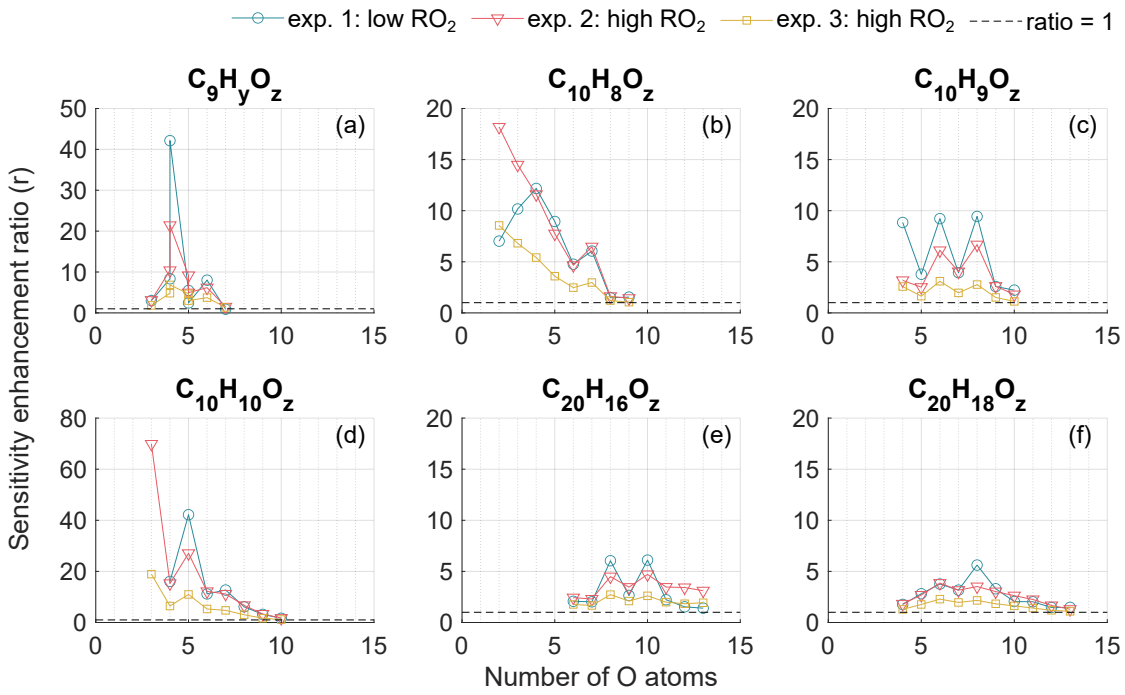

Figure S2. Enhancement in sensitivity for different product groups as function of number of oxygen atoms in the molecule in naphthalene oxidation experiments (exp. 1-3). Panels (a)-(d) show monomers and panels (e)-(f) show accretion products.

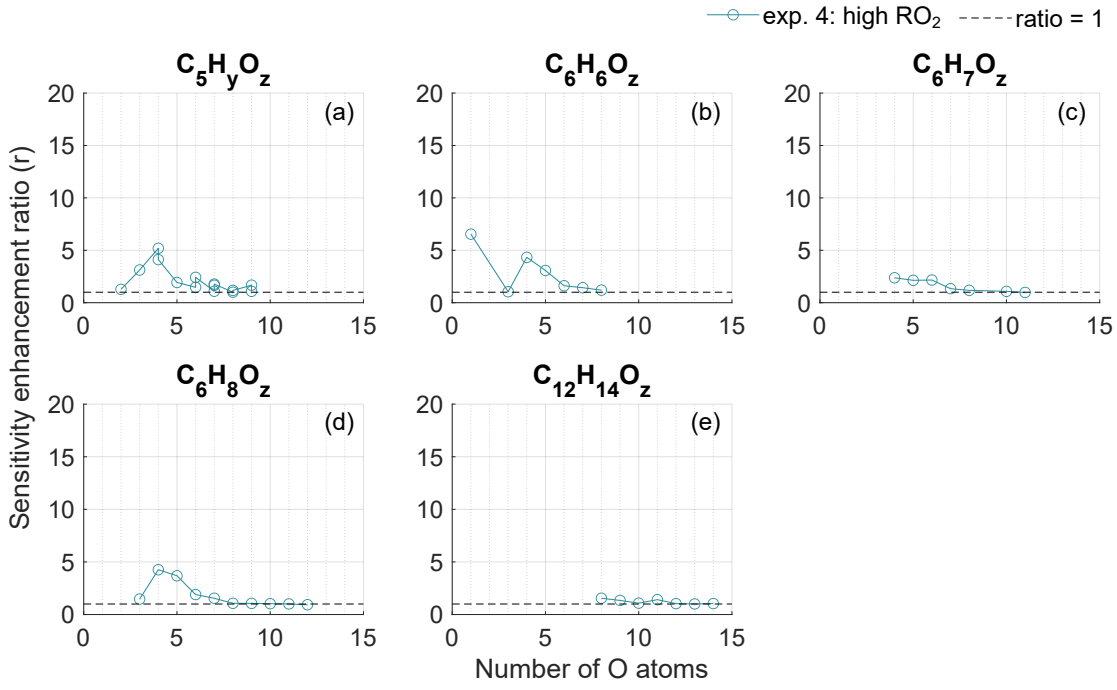

Figure S3. Enhancement in sensitivity for different molecular groups in benzene oxidation experiment (exp. 4).

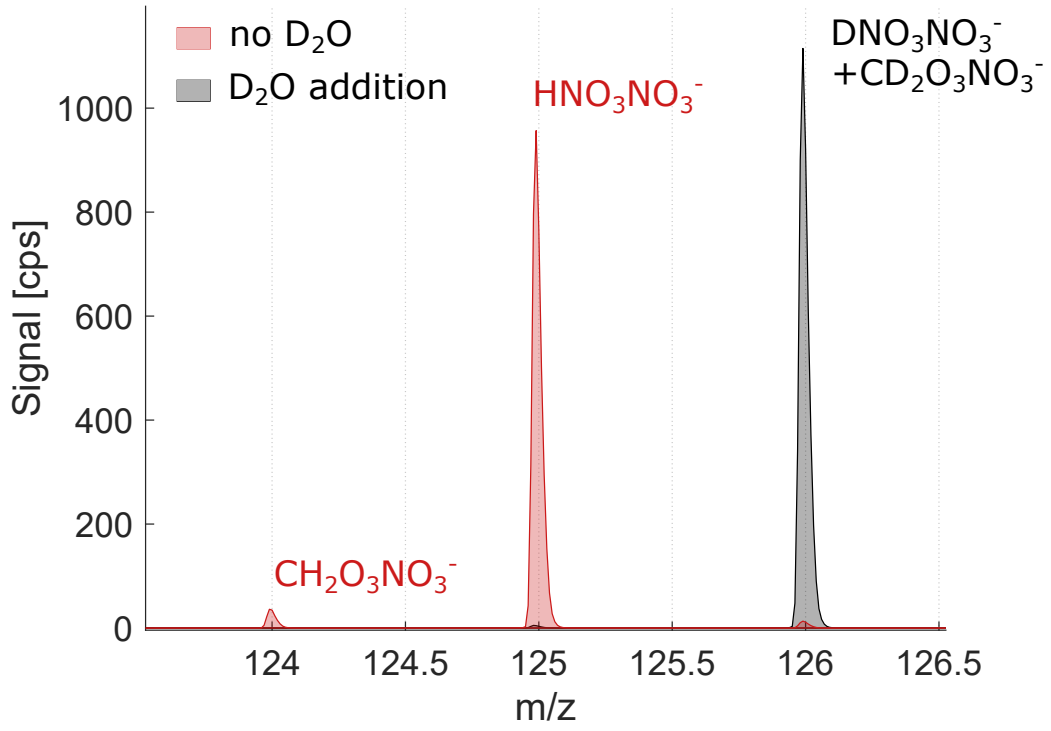

Figure S4. D_2O addition in naphthalene oxidation experiment (exp. 5) displays full conversion of HNO3NO3- to DNO3NO3-. The increase in signal at m/z 126 as compared to m/z 125 is likely due to simultaneous conversion of carbonic acid.

Table S1. Signals (counts per second) for each detected product in naphthalene experiments 1-3. 0/1 indicate the nitric acid flow settings (1=flow on 10 sccm, 0=flow off). All ions are charged negatively and reagent ion NO3 is included into the formula.

Exact mass m/z	Ion composition	Exp 1, 0	Exp 1, 1	Exp 2, 0	Exp 2, 1	Exp 3, 0	Exp 3, 1
222.0408	C10H8N1O5	0.76	0.11	2.42	0.13	2.59	0.30
226.0357	C9H8N1O6	0.28	0.09	1.61	0.52	1.97	1.07
238.0357	C10H8N1O6	1.63	0.16	30.63	2.11	36.23	5.32
240.015	C9H6N1O7	0.63	0.08	3.06	0.29	3.85	0.80
240.0514	C10H10N1O6	1.22	0.00	20.06	0.29	25.57	1.35
242.0306	C9H8N1O7	0.88	0.02	11.99	0.56	15.22	2.22
242.067	C10H12N1O6	0.09	0.03	0.00	0.07	0.30	0.02
254.0306	C10H8N1O7	2.07	0.17	23.50	2.03	29.36	5.42
255.0385	C10H9N1O7	0.26	0.03	1.40	0.44	1.57	0.61
256.0463	C10H10N1O7	4.67	0.29	83.59	5.46	105.40	16.33
258.0255	C9H8N1O8	0.35	0.06	5.08	0.55	6.13	1.31
260.0412	C9H10N1O8	0.22	0.09	1.79	0.36	2.11	0.70
270.0255	C10H8N1O8	4.61	0.52	71.71	9.25	87.19	24.28
271.0334	C10H9N1O8	1.33	0.35	4.98	1.98	5.52	3.38
272.0412	C10H10N1O8	9.71	0.23	125.20	4.63	157.82	14.37
274.0204	C9H8N1O9	3.45	0.43	51.57	8.35	60.34	16.18
286.0204	C10H8N1O9	3.43	0.72	44.05	9.46	53.17	21.51
287.0283	C10H9N1O9	1.62	0.18	5.87	0.96	5.46	1.76
288.0361	C10H10N1O9	2.37	0.21	86.17	7.08	106.16	20.04
290.0154	C9H8N1O10	0.35	0.39	12.86	8.66	15.57	11.59
290.0518	C10H12N1O9	0.52	0.14	6.22	2.47	9.35	5.50
302.0154	C10H8N1O10	13.44	2.22	294.32	45.45	343.83	115.69
303.0232	C10H9N1O10	0.72	0.18	3.54	0.88	4.03	2.06
304.031	C10H10N1O10	6.15	0.48	144.67	12.94	168.77	35.62
318.0103	C10H8N1O11	0.78	0.52	18.94	11.65	23.87	19.76
319.0181	C10H9N1O11	8.47	0.90	23.98	3.59	21.54	7.77
320.0259	C10H10N1O11	2.72	0.44	70.33	10.48	81.02	26.56
334.0052	C10H8N1O12	3.58	2.32	44.13	30.81	46.76	44.40
335.013	C10H9N1O12	1.56	0.60	4.23	1.62	4.31	2.85
336.0208	C10H10N1O12	4.68	1.47	65.50	19.63	70.33	42.35
351.0079	C10H9N1O13	2.81	1.26	6.04	3.36	5.54	4.93
352.0158	C10H10N1O13	1.45	0.87	18.28	10.67	19.49	16.83
384.1089	C20H18N1O7	18.50	10.48	157.49	86.38	200.91	156.29
400.1038	C20H18N1O8	3.63	1.29	82.87	30.79	103.68	58.76
414.0831	C20H16N1O9	0.23	0.11	3.86	1.59	4.90	2.78
416.0987	C20H18N1O9	24.45	6.50	221.31	57.38	269.13	117.74
430.078	C20H16N1O10	0.10	0.05	2.56	1.11	3.21	1.93
432.0936	C20H18N1O10	3.80	1.20	98.34	31.13	114.63	58.40
446.0729	C20H16N1O11	0.36	0.06	4.72	1.05	5.14	1.88
448.0885	C20H18N1O11	3.72	0.66	51.92	14.76	62.30	28.80
450.0678	C19H16N1O12	0.55	0.28	9.50	5.73	10.97	8.68
462.0678	C20H16N1O12	0.17	0.07	4.65	1.34	5.28	2.52
464.0834	C20H18N1O12	4.36	1.32	95.28	31.48	106.73	58.25
478.0627	C20H16N1O13	0.29	0.05	3.77	0.80	3.98	1.53

480.0784	C20H18N1O13	0.77	0.37	29.05	11.06	33.21	20.44
494.0576	C20H16N1O14	0.10	0.04	3.18	0.92	3.48	1.75
496.0733	C20H18N1O14	2.32	1.15	38.28	17.00	40.21	28.49
510.0526	C20H16N1O15	0.05	0.03	1.37	0.40	1.55	0.84
512.0682	C20H18N1O15	0.31	0.21	10.43	6.26	11.11	9.31
526.0475	C20H16N1O16	0.05	0.04	0.81	0.26	0.83	0.43
528.0631	C20H18N1O16	0.61	0.41	7.20	5.54	7.38	6.76

Table S2. Signals (counts per second) for trimer and tetramer accretion products in naphthalene experiment 2 (Figure 9). 0/1 indicate the nitric acid flow settings (1=flow on 10 sccm, 0=flow off). All ions are charged negatively and reagent ion NO3 is included into the formula.

Exact mass m/z	Ion composition	Exp 2, 0	Exp 2, 1
562.1719	C30H28N1O10	0.78	0.11
576.1511	C30H26N1O11	1.59	0.30
578.1668	C30H28N1O11	1.80	0.23
592.1461	C30H26N1O12	2.25	0.40
594.1617	C30H28N1O12	3.43	0.33
608.141	C30H26N1O13	2.76	0.44
610.1566	C30H28N1O13	4.22	0.58
624.1359	C30H26N1O14	3.41	0.74
626.1516	C30H28N1O14	4.07	0.47
640.1308	C30H26N1O15	2.04	0.46
642.1464	C30H28N1O15	2.75	0.44
656.1257	C30H26N1O16	2.19	0.55
658.1414	C30H28N1O16	1.74	0.32
672.1206	C30H26N1O17	0.93	0.31
674.1363	C30H28N1O17	1.03	0.33
690.1312	C30H28N1O18	0.73	0.25
704.1105	C30H26N1O19	0.35	0.13
706.2294	C40H36N1O11	0.62	0.25
722.2243	C40H36N1O12	0.57	0.21
738.2192	C40H36N1O13	1.70	0.46
754.2141	C40H36N1O14	1.35	0.39
770.209	C40H36N1O15	1.77	0.43
786.204	C40H36N1O16	1.05	0.36
802.1989	C40H36N1O17	0.62	0.24
818.1938	C40H36N1O18	0.57	0.20
834.1887	C40H36N1O19	0.27	0.10

Table S3. Signals (counts per second) for each detected product in benzene experiment (exp. 4). 0/1 indicate the nitric acid flow settings (1=flow on 10 sccm, 0=flow off). All ions are charged negatively and reagent ion NO3 is included into the formula.

Exact mass m/z	Ion composition	Exp 4, 0	Exp 4, 1
156.0302	C6H6N1O4	0.77	0.12
160.0251	C5H6N1O5	210.11	164.49
176.0201	C5H6N1O6	12.73	4.08
188.0201	C6H6N1O6	83.36	79.84
189.9993	C5H4N1O7	12.43	2.40
190.0357	C6H8N1O6	3.19	2.16
192.015	C5H6N1O7	29.32	7.13
192.0514	C6H10N1O6	0.39	0.11
204.015	C6H6N1O7	84.05	19.42
205.0228	C6H7N1O7	6.25	2.63
206.0306	C6H8N1O7	240.34	56.40
208.0099	C5H6N1O8	19.30	10.00
220.0099	C6H6N1O8	46.46	15.13
221.0177	C6H7N1O8	2.60	1.22
222.0255	C6H8N1O8	329.39	89.36
224.0048	C5H6N1O9	32.56	22.17
224.0412	C6H10N1O8	0.95	0.94
226.0205	C5H8N1O9	21.00	8.67
236.0048	C6H6N1O9	19.85	12.26
237.0126	C6H7N1O9	1.77	0.82
238.0205	C6H8N1O9	92.92	48.95
239.9997	C5H6N1O10	30.94	28.27
241.0075	C5H7N1O10	3.59	2.16
242.0154	C5H8N1O10	20.79	11.71
251.9997	C6H6N1O10	11.91	8.33
253.0075	C6H7N1O10	2.66	1.99
254.0154	C6H8N1O10	45.13	29.13
255.9946	C5H6N1O11	62.43	62.16
258.0103	C5H8N1O11	6.04	5.16
267.9946	C6H6N1O11	19.51	16.27
269.0025	C6H7N1O11	3.16	2.68
270.0103	C6H8N1O11	94.86	88.87
271.9896	C5H6N1O12	12.59	7.52
274.0052	C5H8N1O12	4.18	3.85
286.0052	C6H8N1O12	39.21	36.95
300.9923	C6H7N1O13	3.23	2.99
302.0001	C6H8N1O13	26.01	25.25
316.9872	C6H7N1O14	2.97	3.03
317.995	C6H8N1O14	8.61	8.52
333.9899	C6H8N1O15	5.81	6.23
348.0572	C12H14N1O11	65.33	42.18
364.0522	C12H14N1O12	20.24	15.09
380.0471	C12H14N1O13	10.17	9.39
396.042	C12H14N1O14	10.66	7.55
412.0369	C12H14N1O15	15.29	14.76

428.0318	C12H14N1O16	4.47	4.44
444.0267	C12H14N1O17	5.15	4.95

Table S4. Regression analysis coefficients presented in Figure 6 of the main text. r is the sensitivity enhancement ratio, O:C is oxygen-to-carbon ratio, OSc is oxidation state of carbon, C* is saturation vapor concentration, and nO is number of oxygen atoms (see Methods in main text for more details).

	Exp.	**VOC**	**Linear model**	**y**	**x**	**a**	**b**	**R^2**
Figure 6a	2	npt	$\log_{10}(y)= ax+b$	r	O:C	-0.59	0.97	0.10
	4	ben	$\log_{10}(y)= ax+b$	r	O:C	-0.31	0.55	0.36
Figure 6b	2	npt	$\log_{10}(y)= ax+b$	r	OSc	-0.33	0.72	0.12
	4	ben	$\log_{10}(y)= ax+b$	r	OSc	-0.15	0.36	0.33
Figure 6c	2	npt	$\log_{10}(y)= ax+b$	r	$\log_{10}(C^*)$	0.035	0.89	0.37
	4	ben	$\log_{10}(y)= ax+b$	r	$\log_{10}(C^*)$	0.027	0.27	0.43
Figure 6d	2	npt	$\log_{10}(y)= ax+b$	r	nO	-0.08	1.22	0.36
	4	ben	$\log_{10}(y)= ax+b$	r	nO	-0.05	0.58	0.48