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Supplementary Information

The fate of plasma-generated oxygen atoms in aqueous solutions: non-equilibrium atmospheric pressure plasmas as an efficient source of atomic $O_{(aq)}$

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SI.1 Reaction records in NDRL/NIST database for ROS

There are 2535 records available for reactions of OH radicals, 944 records for H atoms, 802 records for ozone, 640 for superoxide O_2^-, 301 records for H^+ cations, 291 records for O_2H radicals, 107 for H_2O_2 molecules, 75 for OH^- anions, but currently only 8 records for reactions of O atoms, see Table SI.1 (data retrieved in October 2017).

Table SI.1: The list of ground state $O_{(aq)}$ reactions available in the NDRL/NIST Solution Kinetics Database.

Reactant	Products	Rate constant [$M^{-1}s^{-1}$]	Source of O	Ref.
O_2	O_3	4.0×10^9	photolysis of BrO_3^-, ClO_3^-, or HClO	[5]
H_2O_2	$OH + HO_2$	1.6×10^9	photolysis of H_2O_2 in alkaline aq. sol.	[4]
BrO_3^-	$O_2 + BrO_2^-$	7×10^7	γ-ray irradiated aq. bromate solutions	[3]
BrO_3^-	$O_2 + BrO_2^-$	1.7×10^7	photolysis of BrO_3^-, ClO_3^-, or HClO	[5]
ClO_4^-	Products	$< 6.0\times10^5$	γ- and 184.9-nm-irr. aq. perchlorate	[2]
HO_2^-	$OH + O_2^-$	5.3×10^9	photolysis of H_2O_2 in alkaline aq. sol.	[4]
OH^-	HO_2^-	4.2×10^8	photolysis of H_2O_2 in alkaline aq. sol.	[4]
c-C_5H_8	$H_2C{=}CH_2$	1.2×10^{10}	γ-ray irradiated aq. solutions	[1]

SI.2 Ratios of relative abundances at peak maxima for the most important m/z peaks in the negative sensitivity mass spectra (average of three measurements) of the 0.5 mM phenol solutions.

Table SI.2 summarizes ratios of the most important m/z peaks in the mass spectra of the untreated sample, the sample treated with He/$^{16}O_2$ plasma, and the sample treated with He/$^{18}O_2$. All results are calculated as the average values of the three experiments. In table 1, the changes induced using the heavy oxygen isotope become obvious. The ratios of abundances of phenol hydroxylation products to phenol changes significantly comparing

the normal and labeled treatments. The ratio of unlabeled HQ, CC, and RS (m/z = 109.03), HBQ (m/z = 123.01), and triols (m/z = 125.02) to phenol are always clearly higher for the normal treatment than for the labeled one. Vice versa, the labeled products are dominating the spectrum for the labeled treatment for all detected products. The clearest representation of the changes between the two treatments are the ratios of labeled to unlabeled phenol reaction products, see second part in table SI.2.

Table SI.2: Ratios of relative abundances at peak maxima for the most important m/z peaks in the negative sensitivity mass spectra (average of three measurements) of the 0.5 mM phenol solutions. The masses are rounded to the integer numbers.

Ratio, names	Ratio, masses	treated with $He/^{16}O_2$	treated with $He/^{18}O_2$
diols/phenol	109/93	1.88	0.15
diols (1x ^{18}O)/phenol	111/93	0.01	1.85
HBQ/phenol	123/93	0.56	0.06
HBQ (1x ^{18}O) or triol/phenol	125/93	0.86	0.37
HBQ (2x ^{18}O) or triol (1x ^{18}O)/phenol	127/93	0.01	0.67
triol (2x ^{18}O)/phenol	129/93	0.01	1.24
diols (1x 18O)/diols	111/109	0.005	11.20
HBQ (2x 18O)/HBQ	127/123	0.01	10.86
triol (2x 18O)/triol	129/125	0.01	3

SI.3 Comparison of the ratio of signal maxima for the most important masses in the plasma treated 5 mM phenol solution.

Table SI.2 shows a comparison of the ratio of the maximal values for the two observed peaks in the time-resolved measurements for samples treated with $He/^{16}O_2$ plasma and samples treated with $He/^{18}O_2$ plasma. Each number in the table is an average value from three treatments under identical experimental conditions and multiple runs of each sample by GC-MS. The baseline shift due to the tail of the CC signal has been subtracted from the HQ signal at the retention time of 18.2 min. Additionally, the signal intensities at mass 110 in the labeled treatment have been corrected for the fragment ions appearing

at mass 110 due to fragmentation of the labeled parent ion at mass 112. The fragmentation ratio (3% signal intensity in the case of CC and 15.5% in the case of HQ) have been taken from the fragmentation patterns of the unlabeled spectra shown in Figures SI.4 and SI.6 as the ratio of the signal at m/z = 108 to the signal at m/z = 110.

Table SI.3: Comparison of the ratio of signal maxima for the most important masses in the plasma treated 5 mM phenol solution.

Ratio, names	Ret. time, min	Ratio, masses	treated by He/$^{16}O_2$	treated by He/$^{18}O_2$
CC (1x ^{18}O)/CC	17.2	112/110	0.01	16.7
HQ (1x ^{18}O)/HQ	18.2	112/110	0.01	19.4

SI.4 Detailed plasma source and treatment description

The plasma source used in this work is an earlier version of the COST reference jet (see figure 1 in the article and ref.[41]). It is a capacitively coupled plasma source with two stainless steel electrodes at 1 mm distance. Both electrodes are 30 mm long, 1 mm thick and glued in between two 1.5 mm thick quartz glass plates with vacuum compatible glue giving 1 x 1 x 30 mm^3 plasma volume. One of the two electrodes is powered by a 13.56 MHz sinusoidal voltage with 230V root-mean-square (rms) connected to a commercial RF generator through an impedance matching network. This is the main difference compared to standard COST reference jet, which is powered by a home-made resonance circuit. We have not observed any difference in performance between the two devices up to now. As feed gas, helium with a flow of 1.4 standard liters per minute (slm) is used and admixed with 0.6% of molecular oxygen ($^{16}O_2$) or molecular oxygen isotope ($^{18}O_2$, 99 atom % ^{18}O, Sigma-Aldrich).

The O_2 admixture of 0.6% was previously shown to yield the maximum O density when the O_2 admixture is scanned at a constant voltage of U_{rms} = 230 V. The increase of the

applied voltage (power) increases the O density further. The O atom density was determined to be 8×10^{14} cm^{-3} 4 mm away from the jet nozzle when measured by molecular beam mass spectrometry (MBMS).[43] The oxygen atoms are generated in electron impact dissociation reactions of oxygen molecules. The main loss of O atoms in the gas phase is a three-body recombination with oxygen molecules with helium being the third body.

Plasma treatments of aqueous solutions were performed in a small glass chamber with a closed controlled atmosphere, without contact to the ambient air. The chamber consisted of a small, 6 mL glass cylinder closed by an aluminum cover with an integrated gas exhaust line. The µAPPJ was glued to a polyoxymethylene (POM) polymer plate and mounted on the cover.

Three mL of each solution were treated in the chamber with the plasma at a distance of 4 mm. To avoid possible $^{18}O_2$ contamination in $^{16}O_2$ samples, the treatments were first performed with He/$^{16}O_2$ plasma, and the bottle with $^{18}O_2$ was connected to the system after these measurements and following extensive pumping of the gas supply system.

The handling of the solutions after the treatments has been as follows. Directly after treatment, 2 mL of the plasma treated solutions were inserted into plastic vials (Eppendorf Tubes®) and were brought to the high-resolution mass spectrometer (Applied Microbiology group at Ruhr-University Bochum) for analysis, which took place within few hours after the treatment. The remaining part (slightly less than 1 mL due to water evaporation during the treatment) was sent to Loughborough University for analysis with GC-MS, which took place on the next day. Each treatment has been repeated three times.

SI.5 Analysis of aqueous chemistry products: mass spectrometry

The mass spectrometry measurements have been performed within few hours after the treatment. Liquid samples (untreated 0.5 mM phenol solutions and solutions exposed to 4 min of plasma treatment) were directly injected into a Synapt G2-S-HDMS^E mass spectrometer (Waters, Milford, Massachusetts, USA) in combination with an ESI-LockSpray-Source (Waters). Spectra were recorded for 2 min in negative ionization mode with the following settings: capillary voltage = 3 kV, cone voltage = 40 V, source temperature = 100°C, cone gas flow = 50 L/h, desolvation gas flow = 500 L/h, and desolvation temperature = 150°C. MS spectra were recorded within a mass range of 50-600 m/z with a scan time of 1 s. Leucine-encephalin was injected every 60 s as a lock mass using a capillary voltage of 3 kV. Data were recorded and analyzed using the MassLynx software (Waters, version 4.1 SCN932).

In negative ionization mode, compounds lose one hydrogen atom during the ionization process and are then accelerated by the electric field as negatively charged ions. Therefore, all the measured and presented masses will be one amu lower than the mass of the originally injected species. The mass spectrum of phenol (Figure 2a) is characterized by a peak of m/z = 93.03, corresponding to the mass of the phenol molecule C_6H_6O (mass 94 amu). This peak is taken as a reference for the signal intensity in all the MS spectra reported in the paper. The reproducibility of the result for the three treatments is shown on an example of He/$^{16}O_2$ treatment in Figure SI.1.

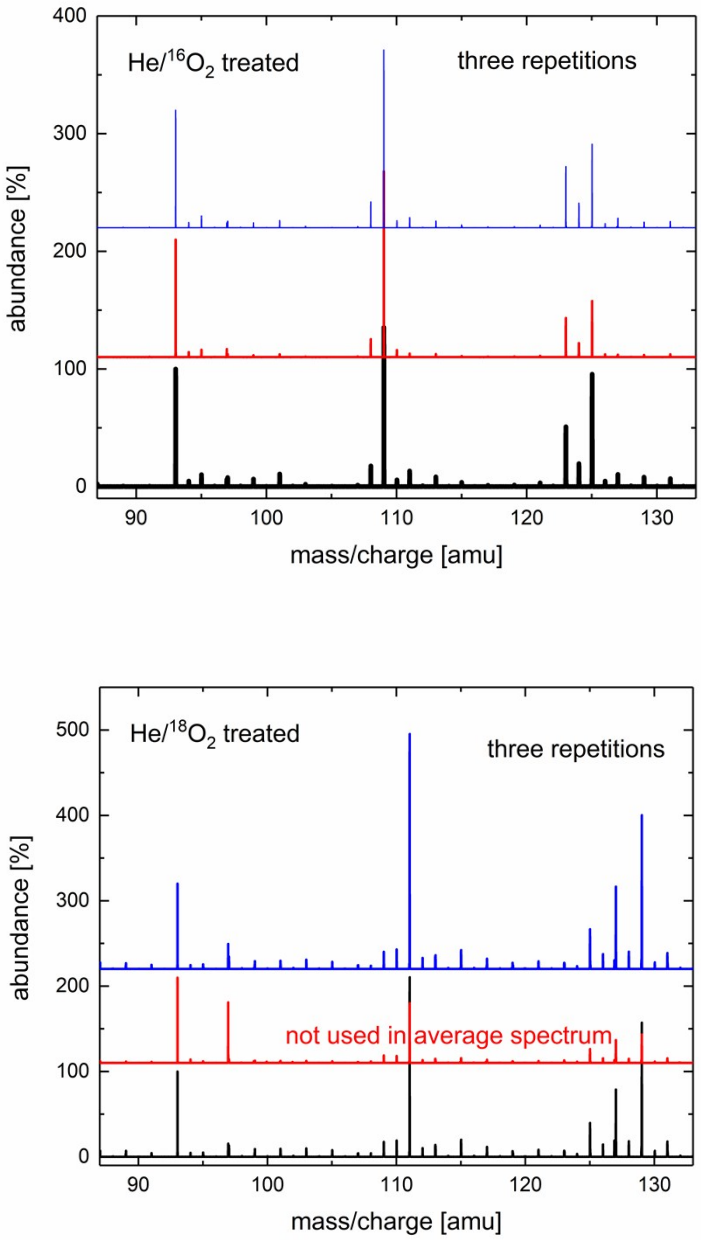
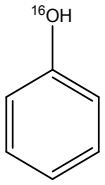
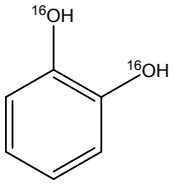
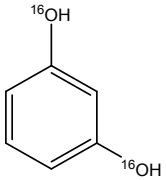
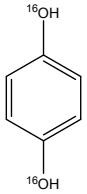


Figure SI.1. The comparisons of the three MS spectra, normalized to the phenol peak, as obtained for the three repetitions of the treatment for both normal and labeled oxygen. Figure 2b) and c) in the article shows the average of these spectra. One repetition of the He/$^{18}O_2$ treatments (red spectrum) shows some unknown impurity at m/z of 97 amu and clearly different amounts of detected products. This spectrum was excluded from the average.

SI.6 Analysis of aqueous chemistry products: gas chromatography-mass spectrometry

Gas chromatography-mass spectrometry analysis have been performed one day after the treatment. However, repeated measurements have shown that phenol byproducts are stable and detectable by GC-MS after plasma treatment for days. Liquid samples (untreated 5 mM phenol solutions and solutions exposed to 8 min of plasma treatment) were analyzed using an Agilent 7890A gas chromatograph and Agilent 5975C® mass spectrometer. Pre and post injection washes of the syringe were carried out using 8 x 8 μL of methanol followed by pre injection washes of the syringe using 4 x 8 μL of the sample. The final injection volume of sample was 1 μL. The inlet was operated in splitless mode: a temperature = 150 ˚C, pressure =16.909 psi and a flow rate of 1 mL/min of helium. The capillary column was a DB5-MS Agilent® 60 m x 250 μm x 0.25 μm with an initial temperature of 50 ˚C for 5 min followed by a ramp temperature of 10 ˚C/min for 25 min. The electron impact ionization was performed with 70 eV electron energy. Mass monitoring was done between 33 m/z and 350 m/z so that the whole mass range of interest can be monitored in the low resolution scan. Single ion monitoring (SIM) was performed on 94 m/z and 96 m/z for the first 16 minutes to monitor phenol in high resolution. From 16 min onwards SIM was performed on 110 m/z, 112 m/z, and 114 m/z to monitor different diols in high resolution. The detection limit of the GC-MS was worse than that of the MS, and therefore higher phenol concentrations (5 mM instead of 0.5 mM) and longer plasma treatments (8 min instead of 4 min) were used to prepare samples for GCMS diagnostics.

Table SI.4: Retention time of phenol, catechol, resorcinol and hydroquinone.

	 phenol	 catechol	 resorcinol	 hydroquinone
Retention time (min)	12.7	17.2	18.3	18.2

Phenol, catechol, resorcinol and hydroquinone were obtained from Sigma-Aldrich and ran through the GC to determine the retention time of each compound for our experimental setup. The retention times are shown in Table SI.2. The relative sensitivity of the GC to each of these compounds can be infer from the GC trace shown in Figure SI.2, where a solution 500 μM of phenol, catechol, resorcinol and hydroquinone was ran through the GC.

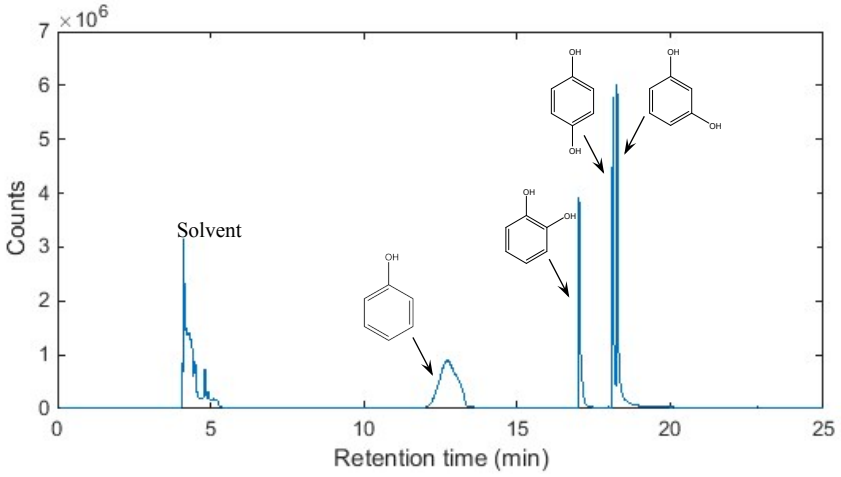


Figure SI.2. GC trace of a 1mM phenol, catechol, resorcinol and hydroquinone solution.

The mass spectra of each of the peaks on the chromatograph are shown below.

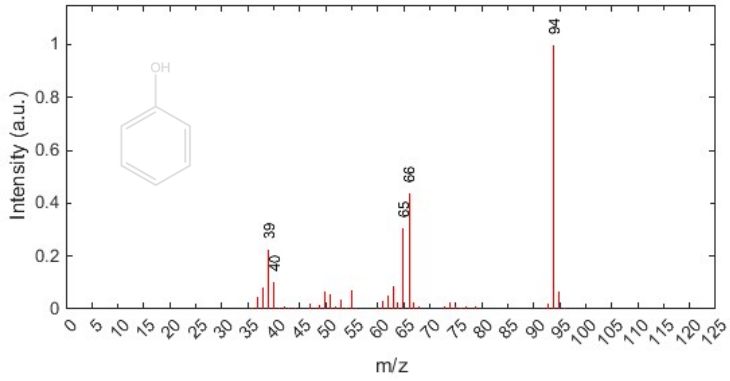


Figure SI.3. Mass spectrum of phenol

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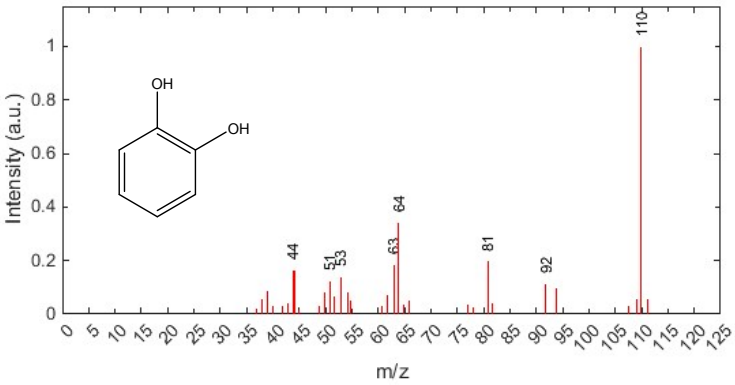


Figure SI.4. Mass spectrum of catechol.

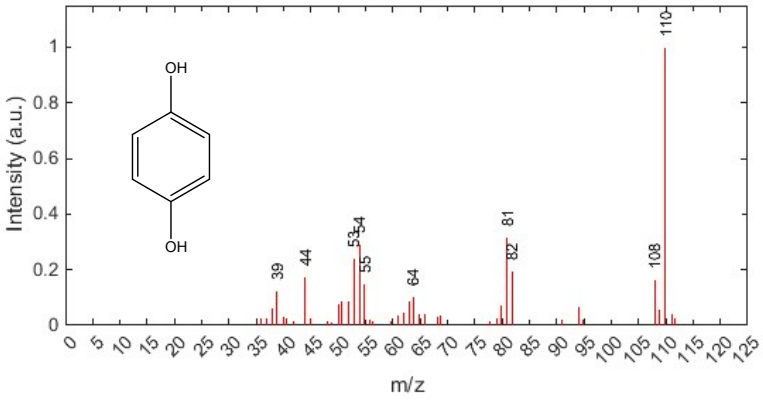


Figure SI.5. Mass spectrum of resorcinol.

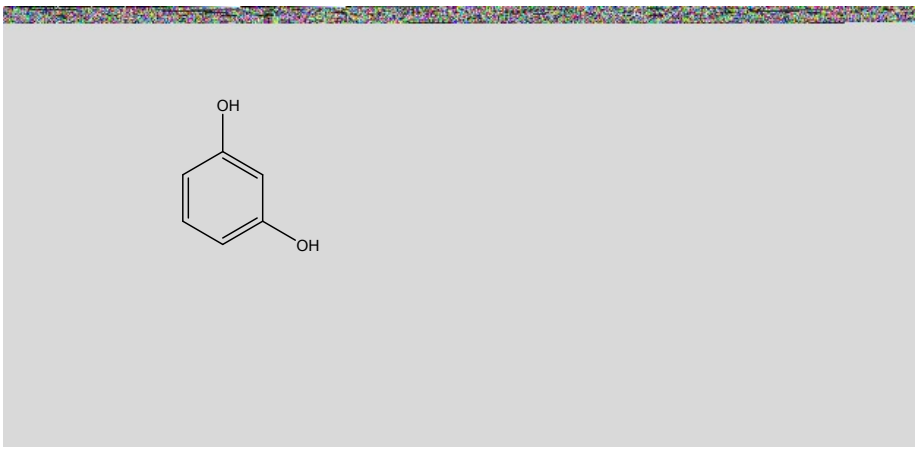


Figure SI.6. Mass spectrum of hydroquinone.

SI.7 Gas chromatographs of untreated and treated phenol solutions

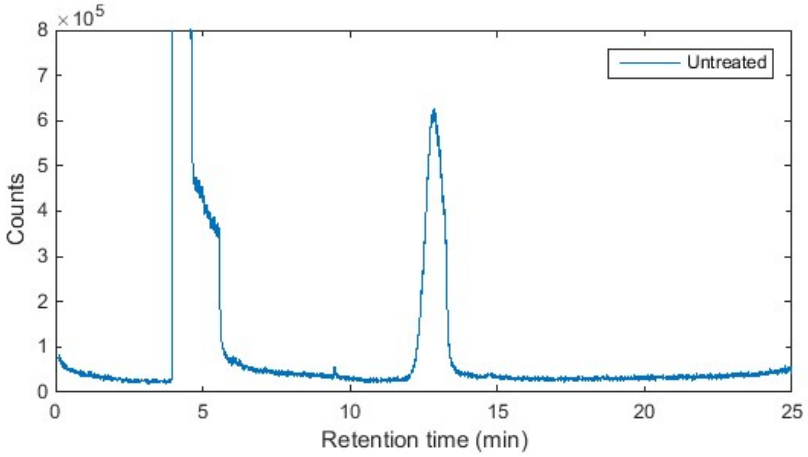


Figure SI.7. GC trace of an untreated 5mM phenol solution.

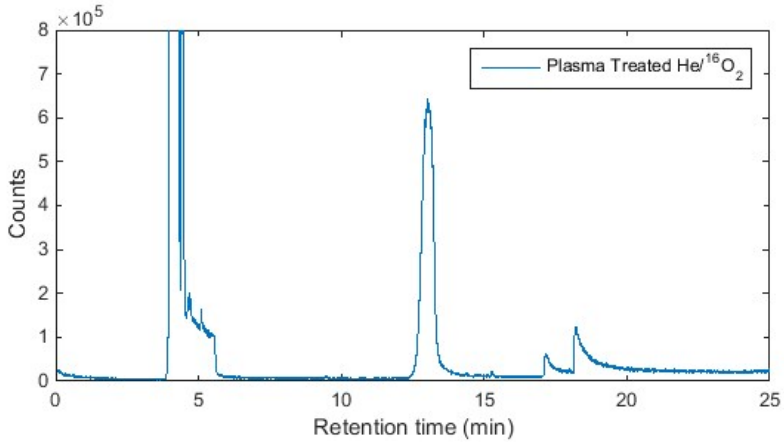


Figure SI.8. GC trace of a He + $^{16}O_2$ plasma treated 5mM phenol solution. Catechol and hydroquinone are clearly observable but resorcinol, if present, it is in negligible concentration.

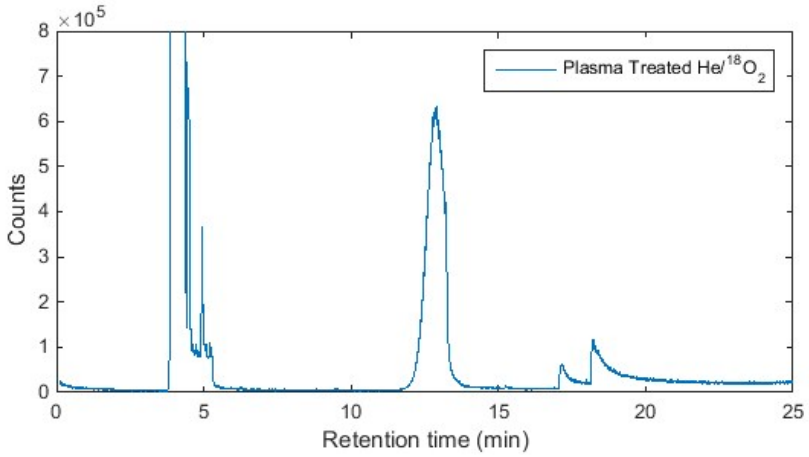
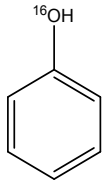
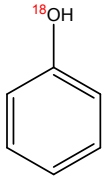
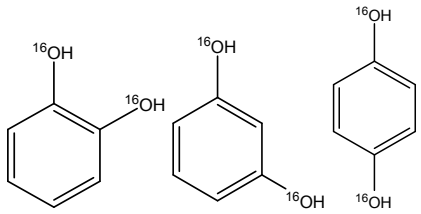
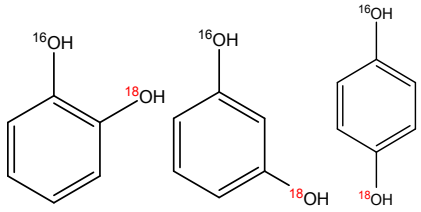
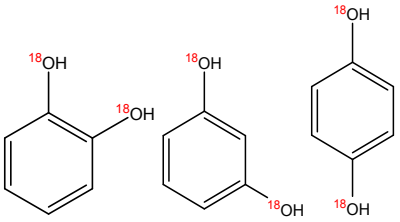


Figure SI.9. GC trace of a He + $^{16}O_2$ plasma treated 5 mM phenol solution. Catechol and hydroquinone are clearly observable but resorcinol, if present, it is in negligible concentration.

Table SI.5: Masses/compounds monitored in SIM mode:

Mass (amu)	Compounds
94	
96	
110	
112	
114	

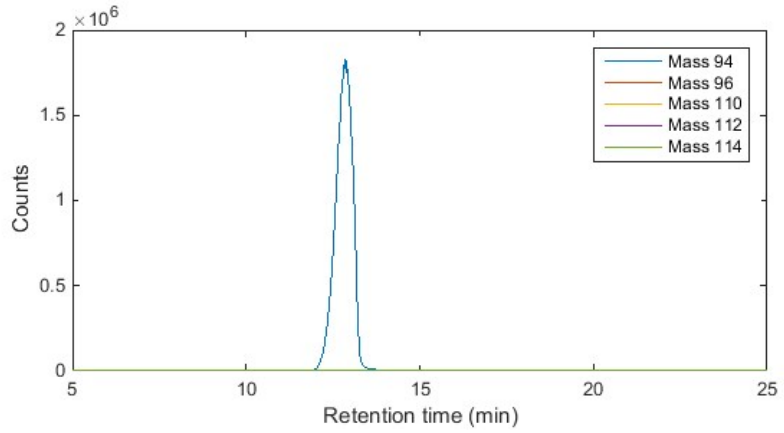


Figure SI.10. Untreated sample – 5 mM phenol solution: SIM GC trace of relevant ions.

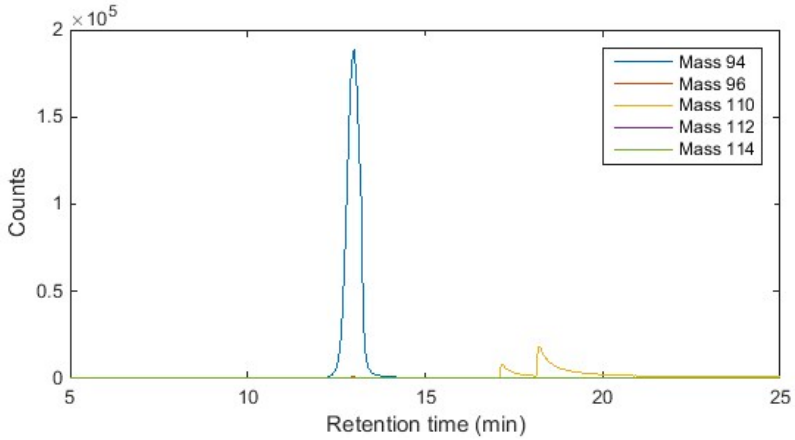


Figure SI.11. Treated sample – 5 mM phenol solution exposed to He/$^{16}O_2$ plasma for 8 minutes: SIM GC trace of relevant ions.

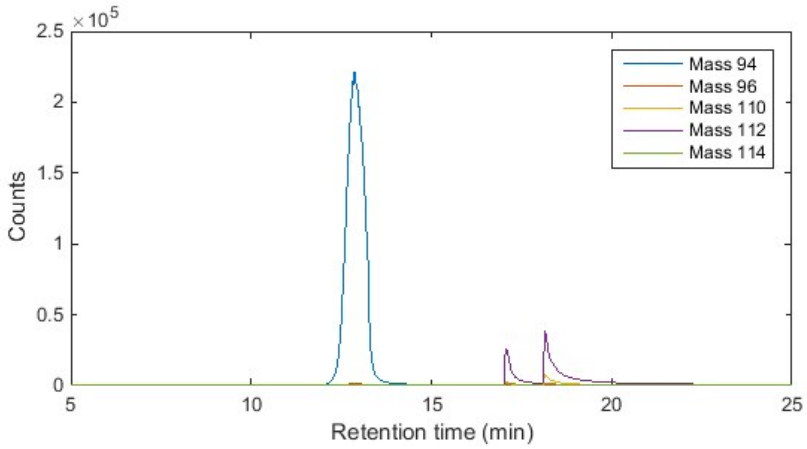


Figure SI:12. Treated sample – 5 mM phenol solution exposed to He/$^{18}O_2$ plasma for 8 minutes: SIM GC trace of relevant ions.