

Electronic Supplementary Information

Improving oxidation efficiency through plasma coupled thin film processing

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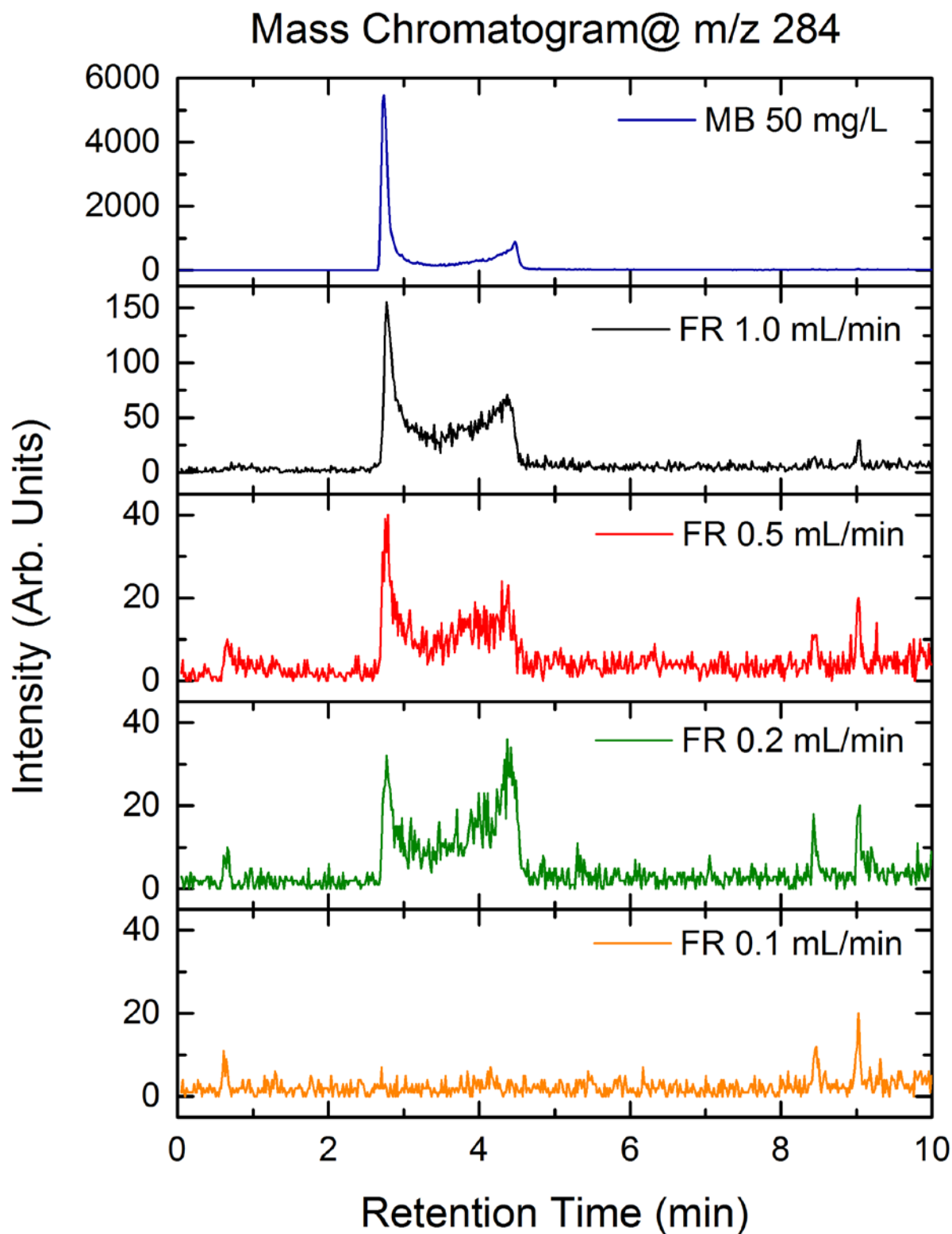
1. Liquid chromatography mass spectrometry

To confirm the degradation of the methylene blue (MB) through the plasma treatment, samples plasma treated at 8000 rpm using different flow rates were analysed using liquid chromatography mass spectrometry. The experimental details for this analysis is contained in section 2.

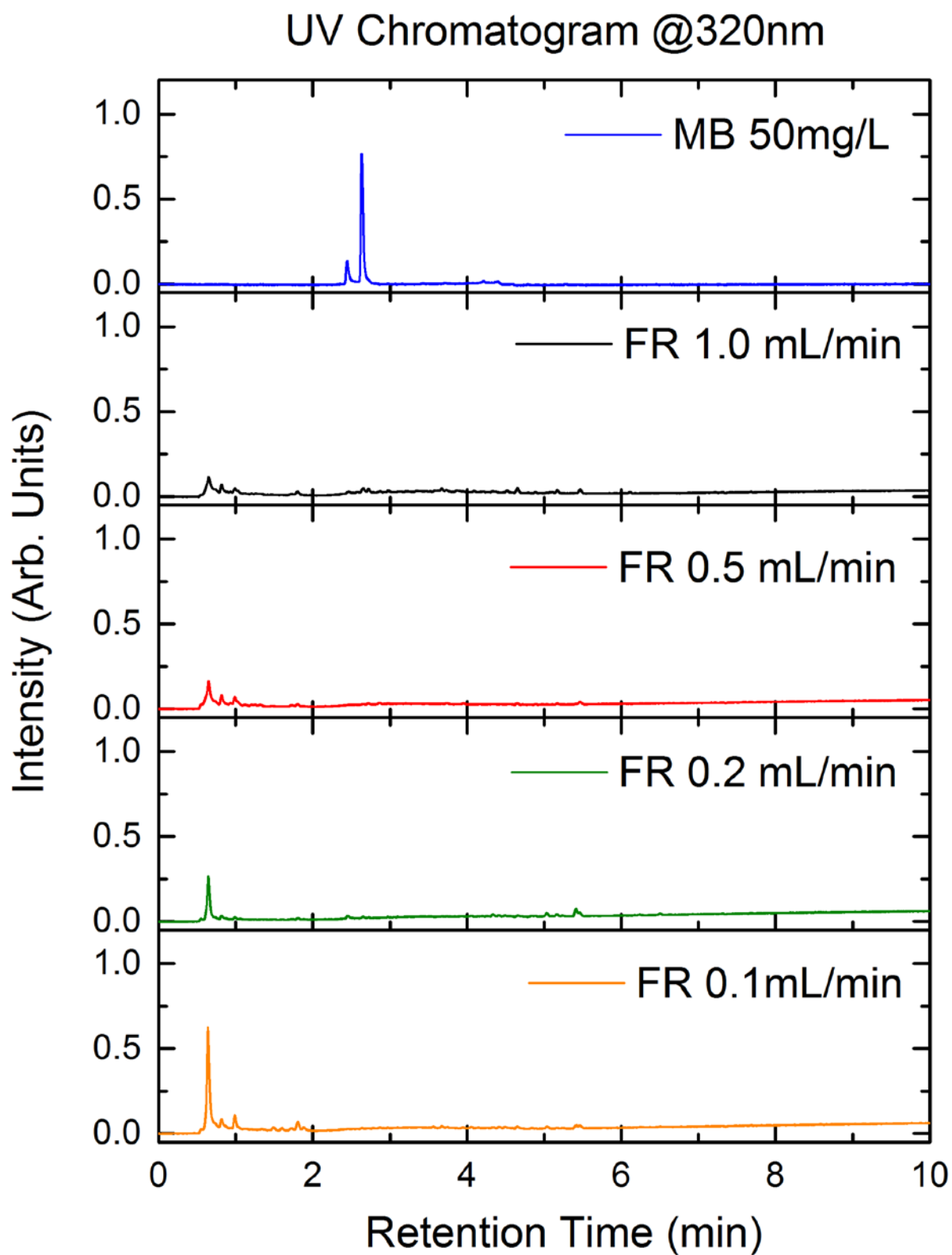
Mass chromatograms for the methylene blue (MB) positive ion, $m/z = 284$ are shown in SI Fig. 1. Here we can observe removal of the MB from solution at rates consistent to that obtained through analysis of the characteristic absorption peak in the 550-710 nm range.

The MB degradation is further supported by UV chromatograms at 320 nm (SI Fig. 2) that reveal that even for the fastest flow rate of 1.0 mL/min (shortest plasma exposure), the majority of the MB in solution has been degraded through the plasma treatment. At this flow rate, we also do not see any strong evidence for the formation of other degradation products. As the flow rate is reduced, to increase the residence time of the solution in the plasma region, we see an increase in species not retained in the column. This observation is consistent with a larger number of ions being formed in solution through the increased exposure time to the plasma and a modification of the solution pH [1,2].

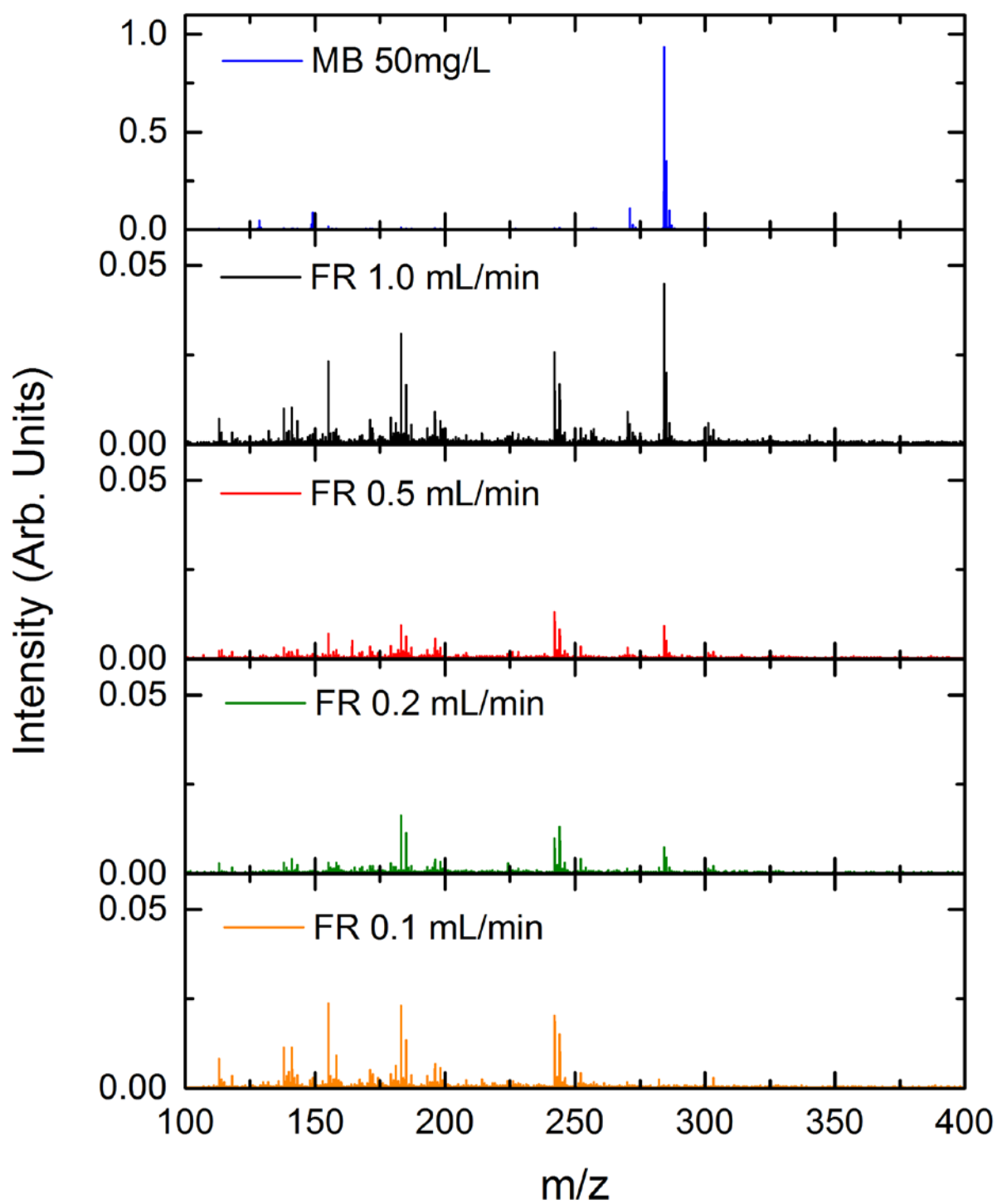
A mass spectrum was obtained at 2.7 min retention time for the MB stock solution and plasma treated samples (SI Fig. 3). Here the 2.7 min retention time corresponds to the maximum absorption peak for the MB stock solution. The mass spectra for the different flow rates (plasma exposure time) confirm that the MB remaining in solution decreases with increased exposure to the plasma. These mass spectra also reveal that there is minimal degradation products formed. This suggests that the degradation of MB proceeds rapidly in the thin-film when exposed to the plasma.



SI Fig. 1: Example mass chromatograms at m/z=284 for MB stock solution (50 mg/L), and plasma treated MB solutions at 8000 rpm for flow rates of 1.0 mL/min, 0.5 mL/min, 0.2 mL/min and 0.1 mL/min.



SI Fig. 2: Example UV Chromatograms at 320nm for MB stock solution (50 mg/L), and plasma treated MB solutions at 8000 rpm for flow rates of 1.0 mL/min, 0.5 mL/min, 0.2 mL/min and 0.1 mL/min.



SI Fig. 3: Mass spectra at 2.7 min retention time for the MB stock solution, and plasma treated MB solutions at 8000 rpm for flow rates of 1.0 mL/min, 0.5 mL/min, 0.2 mL/min and 0.1 mL/min.

2. LCMS experimental details.

- **Electrospray**

The ESI mass spectra were obtained on a Waters Synapt HDMS (Waters, Manchester, UK). Mass spectra were obtained in the positive ion mode with a capillary voltage of 3 kV and a sampling cone voltage of 40 V. The other conditions were as follows: extraction cone voltage, 4.0 V; ion source temperature, 80 °C; desolvation temperature, 350 °C; desolvation gas flow rate, 500 L/h. Data acquisition was carried out using Waters MassLynx (V4.1). Mass spectra were acquired in the V resolution mode over a mass range of m/z 100–800 using continuum mode acquisition. Mass calibration was performed by infusing sodium formate solution (0.5 mM, 1:9 (v/v) water:isopropanol).

- **Sample Analysis**

LC separation was provided by a Waters Acquity UPLC (Waters, Milford, USA)

PDA data also acquired via Acquity PDA.

Data was acquired by the Masslynx Software (v4.1)

Liquid Chromatography

Column: Waters Acquity UPLC BEH C18, 1.7 μ m, 2.1 x 50 mm

Flow rate: 0.2 mL/min

Solvent A: 0.5 % aqueous formic acid

Solvent B: Acetonitrile

Injection Volume (μ L): 1

Pump Gradient Timetable

Time	A%	B%
0	95	5
1	95	5
10	0	100
15	0	100
15.5	95	5
20	95	5

PDA: 190 to 400 nm

3. Conversion efficiency and yield per energy input

In assessing reactor performance, it is necessary to consider conversion efficiency and yield per energy input. Here conversion is expressed as,

$$C = \frac{(C_0 - C_f)}{C_0} \times 100\%.$$

In a traditional batch reactor for plasma chemical processing, the energy efficiency of a reactor is often assessed through the yield per energy input, which is defined through:

$$Y = \frac{V (C_0 - C_f)}{P t}$$

Here, V is the volume of fluid treated, t is the treatment time, P is the power consumed, while C_0 and C_f are the initial and final concentration of the material processed respectively. For a continuous flow reactor, the yield per energy input becomes:

$$Y = \frac{(C_0 - C_f)}{P} FR,$$

where FR is the flow rate.

The degradation of MB has been previously studied in a number of batch-type plasma reactors, and give maximum yields of 4.6 - 5 g.kWh⁻¹ (90% conversion) [3,4]. Grabowski *et al* [4] further quantified the efficiency of other reactor technologies, such as sono-luminescence (0.006 g.kWh⁻¹)[5] or corona in water discharges (0.04 -1.2 g.kWh⁻¹) [6]. It is important to note that in many of these investigations, gas flows of either pure or mixed gases have been used, such as N₂, O₂, Ar, O₃, and acid, base or catalysts have been added to the solution to improve the degradation efficiency [7]. It is also important to note that the quoted yield per energy input often decreases as conversion increases, as in Anghel *et al* [7]. These factors complicate the assessment of the overall reactor performance.

In the present reactor our typical power consumption is 146.5 W (Plasma 37.5W, VFD Motor 100W, Pump 10W). When obtaining 90% conversion, we obtain yields of 0.004 – 0.009 g.kWh⁻¹. In the present investigation we wished to investigate how the liquid film thickness influenced conversion efficiency, and have therefore not attempted to optimise the yield per energy input of our prototype reactor. It is worthy to highlight that there are number of features which can improve the efficiency of a VFD plasma reactor, such as increasing the size of the plasma region where the solution is treated, increasing the plasma volume to produce more active species, and changing the discharge settings to optimise the degradation efficiency. These features should be examined in parallel with scaling the VFD design to accommodate larger flow rates. This, in particular, is important as yield per energy input is directly proportional to the flow rate.

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