## Supplementary information for: LED controlled flow photolysis for concentration gradients in microfluidic systems

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## Non linearity

Some non-linearity in the relation of LED current to generated [HCI] and is likely to result from the changing concentrations of desyl chloride and its photoproducts at different LED currents. As the current is increased, the concentration of unreacted desyl chloride decreases whilst the competing absorption of radiation by organic photoproducts becomes more and more significant. Some absorbing photoproducts may be inert whilst others may themselves undergo acid-releasing photolysis.<sup>[1]</sup> Another potential explanation for this non-linearity is the fact that the radiation intensity is likely to vary considerably throughout the cross-section of the photoreaction cell due to the imperfect emission pattern, refraction, reflection and absorption by desyl chloride and its photoproducts. Therefore it could be that some regions of the cross-section have achieved full conversion at moderate LED currents and that further increases in current lead to photolysis in smaller and smaller regions of the photoreaction cell correlated with current.<sup>[2]</sup>

## Methods

The eluent was 50% w/w acetonitrile (HPLC grade, BDH) with 2.0 mM Desyl Chloride (Alfa Aesar, UK) and 0.24 mM HCl (37%, Sigma-Aldrich). Eluent flow was controlled by an Agilent 1200 series capillary pump G1376A (including 1200 series vacuum degassing unit G1379B). The reported flow rate of 2.3  $\mu$ L/min was confirmed by collecting eluent to measure output volume over time.

The photoreaction cell was a 3 cm section of 1.0 mm ID polyimide coated fused silica tube (Polymicro Technologies, Arizona). The polyimide coating was burned off the tube in the section that was exposed to radiation. An Araldite epoxy adhesive (Selleys, Australia) was used to join the photoreaction cell with fused silica capillary at either end. The cell was rested in a small v-shaped fold of steel to hold it in place and to reflect backward any radiation that was transmitted through the cell.

Three UVTOP-39BL 270 nm and one UVTOP-39BL 290 nm LEDs (Sensor Electronic Technology, Inc.) were connected in series and were powered by a supply with a variable current limiting system with a maximum of 24 mA that was prepared in-house. The LEDs were attached to an XYZ stage and were focussed directly onto the photoreaction cell from above.

The separation column was prepared by packing 25 cm of 330 µm ID PEEK tubing with SCS1 weak cation exchange packing material (Dionex Corporation, California).

The suppressor column was prepared by forming a porous polymer monolith based on the recipe of Preinerstorfer *et al.*<sup>[3]</sup> The composition of the reaction solution was 30% w/w cyclohexanol (99%, Merck)), 30% w/w 1-dodecanol (98%, Sigma-Aldrich), 24% w/w glycidyl methacrylate (97%, Aldrich)) and 16% w/w ethylene dimethacrylate (98%, Aldrich) with 1% w/w AIBN (supplier). The ingredients were sonicated and purged with nitrogen for 10 minutes and then were infused into a length of 250  $\mu$ m ID polyimide coated fused silica capillary (Polymicro Technologies, Arizona) which had been vinylised on the inner surface by a widely used method.<sup>[4]</sup>

Quaternary ammonium groups were then formed by reacting the column with triethylamine (98%, Fluka) at 30  $\mu$ L/hr in a column heater at 70 degrees C for 2 hours and at 60 degrees C for 6 hours based on several reports of amine functionalisation of materials with pendant glycidyl groups.<sup>[3, 5]</sup>

An EDAQ conductivity detector module (eDAQ Pty Ltd, Australia) was operated directly downstream of the suppressor column on 75  $\mu$ m ID polyimide coated fused silica capillary. The data was recorded using a Powerchrom A/D convertor with Powerchrom V2 Software (eDAQ Pty Ltd, Australia). The EDAQ settings for the cation exchange chromatography were 100 V amplitude, 1200 KHz with no offset or output gain but with headspace gain switched on.

A simpler set up was used for the calibration experiments which did not require the separation or suppressor columns. The conductivity detector was operated on a section of 75  $\mu$ m ID polyimide coated capillary directly downstream from the six port injector which led directly to waste. In order to get a linear response for the [HCl] calibration curve the eDAQ settings were changed to 60 V amplitude and 800 KHz frequency with no offset and no headspace gain or output gain. A calibration curve with R<sup>2</sup> = 0.9991 was obtained by spiking the eluent with different concentrations of HCl. The conversion from conductivity to [HCl] relies on the assumption that H<sub>3</sub>O<sup>+</sup> and Cl<sup>-</sup> were the only ionic photoproducts, which is a reasonable assumption given that no other conceivable photoproducts are likely to have been charged in the acidic solution (pH < 3.7).

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