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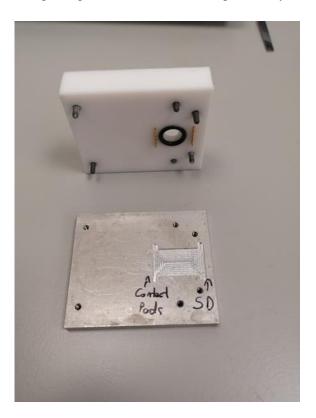
University College Cork, Ireland Coláiste na hOllscoile Corcaigh

Supplementary Material – Electrochemical Detection of Free-Chlorine in Water Samples Facilitated by *in-situ* pH Control using Interdigitated Microelectrodes

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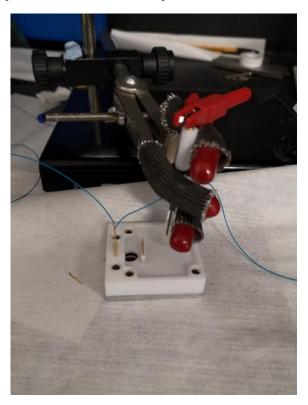
Figures 1 - 3 show the experimental set-up used in each electrochemical measurement. Figure 1 shows the chip holder when it is open. The aluminium base holds the chip in place without allowing for any movement during measurements. The teflon lid has pins to allow electrical contact to the contact pads and has an o-ring to prevent leakage of solutions. Figure 2 shows the assembled set-up, showing the top side of the pins and the teflon holder. The teflon lid facilitates up to 5 mLs of solution with the hole allowing for contact to the electrode arrays. Figure 3 is an image of the working electrochemical set-up where an external reference electrode is used for analysis. This electrode is clamped in place with a retort stand to prevent any movement during analysis.



Supplementary Figure 1: device holder for use in electrochemical measurements. The chips are inserted with the round contact pads on the left and the SD connections on the right. The lid shows the underside of the pins and the o-ring.

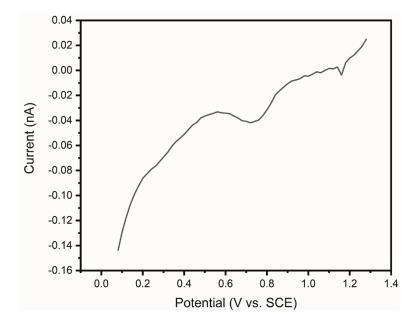


Supplementary Figure 2: The topside of the lid showing the pins that are connected to the relevant terminals of a potentiostat. The hole enables liquid contact to the electrodes.



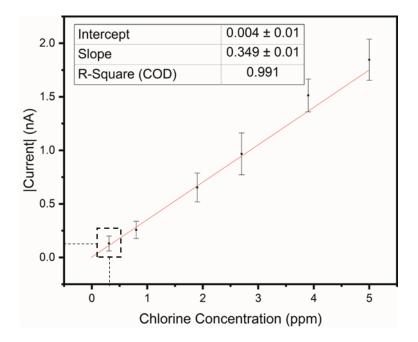
Supplementary Figure 3: The set up used for electrochemical measurements showing the pins connected and an external SCE reference electrode in solution. The reference electrode is held in place using a retort stand.

Figure 4 shows the LSV of the unknown tap water sample. This scan is shown here in isolation to prevent any loss of clarity. The gold oxide reduction peak is visible at 0.75 V, which were seen in the other scans with greater intensity.



Supplementary Figure 4: The unknown tap water scan shown in figure 8 (A) of the manuscript.

Figure 5 is a calibration plot based on the actual values of chlorine in the tap water solutions based on the DPD colorimetric method. Good linearity with an R^2 of 0.991 was observed and a sensitivity of 0.349 nA/ppm was measured. Figure 6 shows a table with the estimated chorine concentrations, and the real chlorine concentrations.



Supplementary Figure 5: A calibration plot based on the actual concentrations of free chlorine in tap water, measured using the DPD colorimetric method. Included is the measured concentration of the tap water unknown sample, which is highlighted by the dashed box

Measured conc.
0.3 ppm
0.8 ppm
1.9 ppm
2.7 ppm
3.9 ppm
5.0 ppm

Supplementary Figure 6: Comparison of the prepared concentrations and the measured concentrations of the tap water samples. The measured concentrations are the values used in the calibration shown in supplementary figure 5.