SUPPLEMENTARY INFORMATION

Detection of free chlorine in water using graphene-like carbon based chemiresistive sensors

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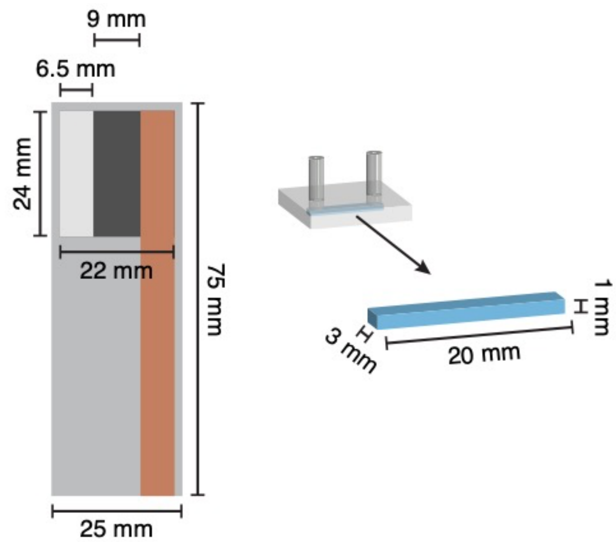
Table of Contents

Figure S1. (a) Dimensions of the sensor components and the flow channel. The exposed area of the GLC in the dip sensors after masking the contacts with PDMS is approximately 8 × 22 mm. (b) Experimental setup for measurement.

(a)



(b)

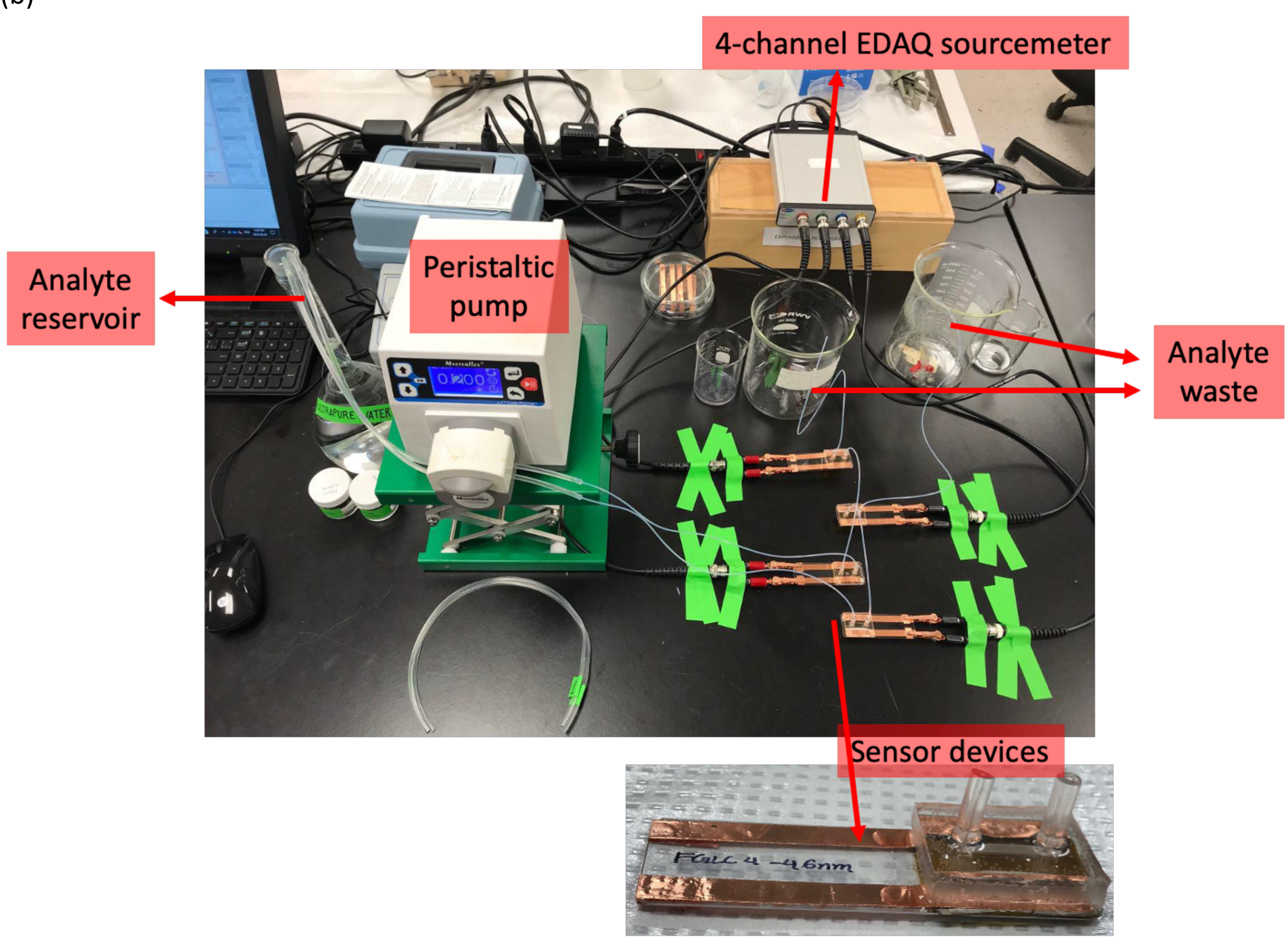
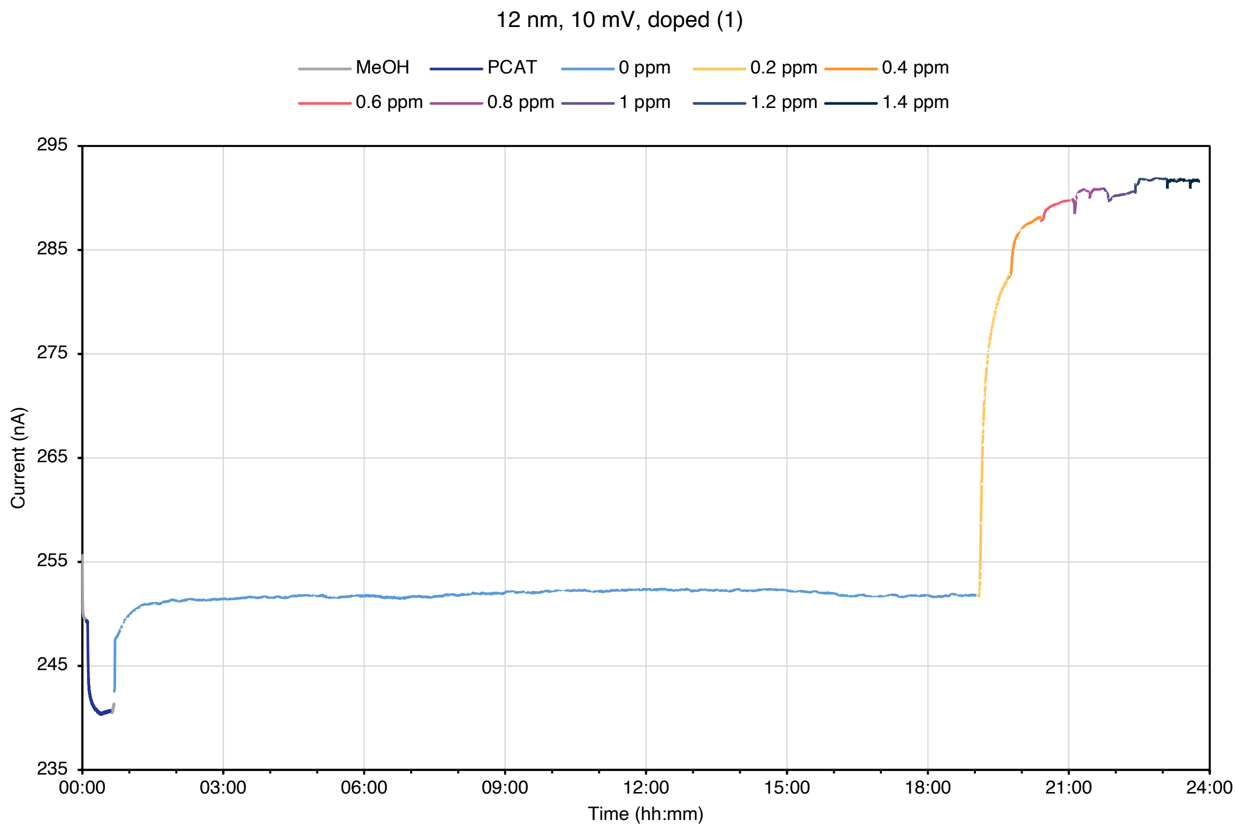
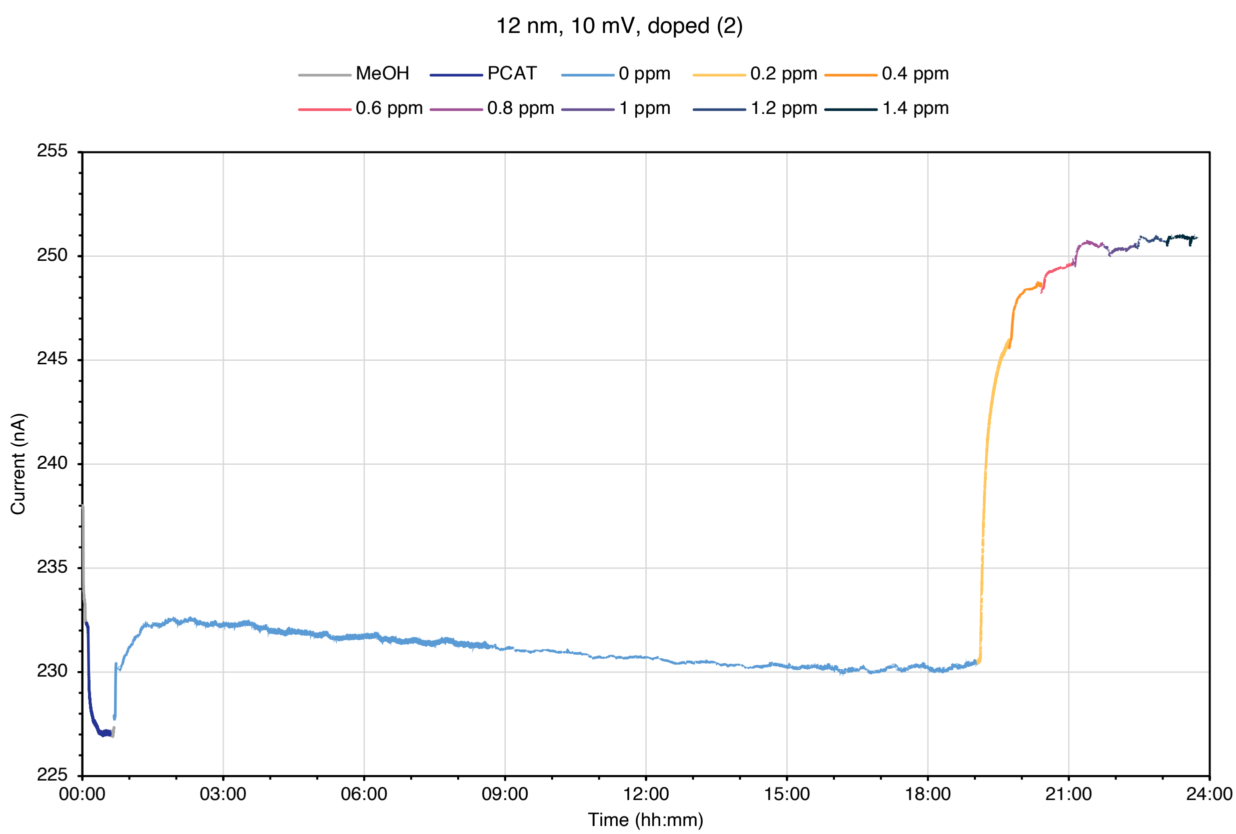
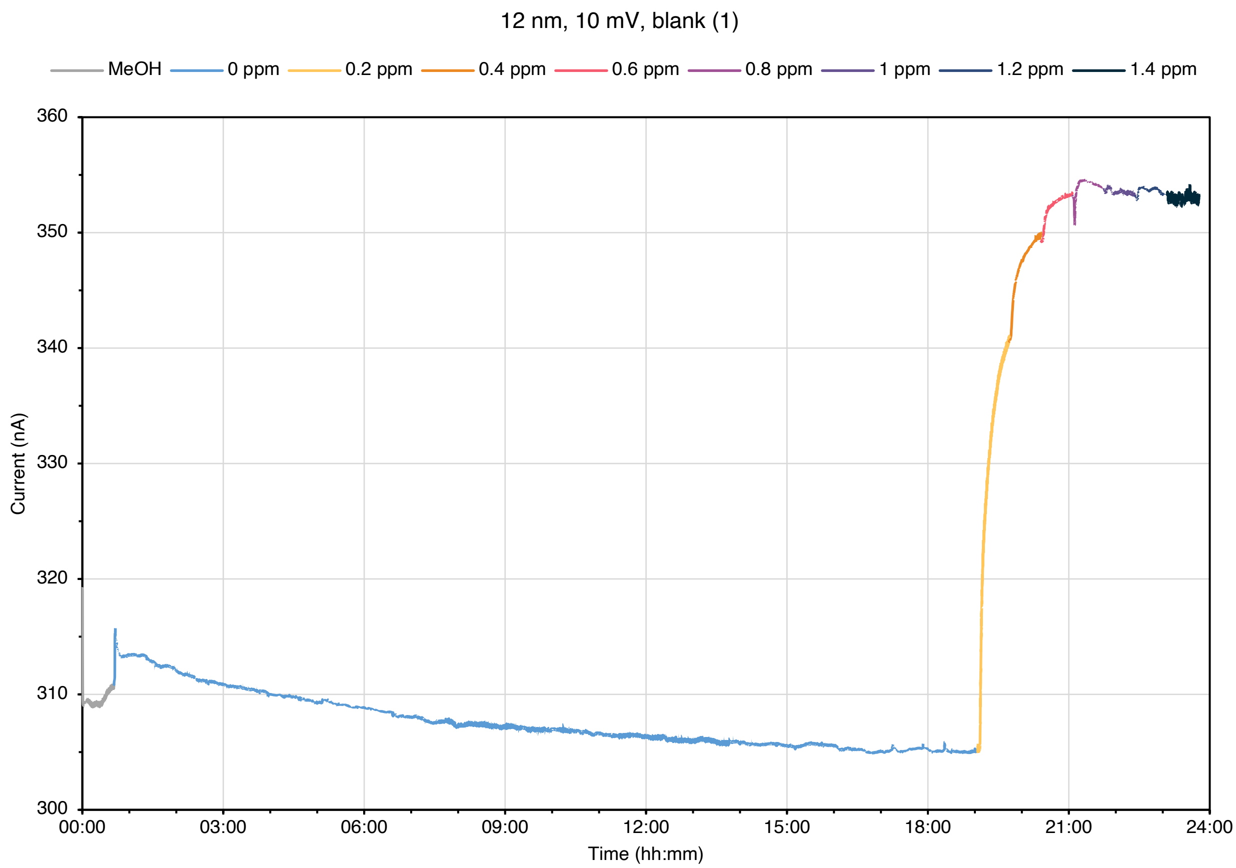
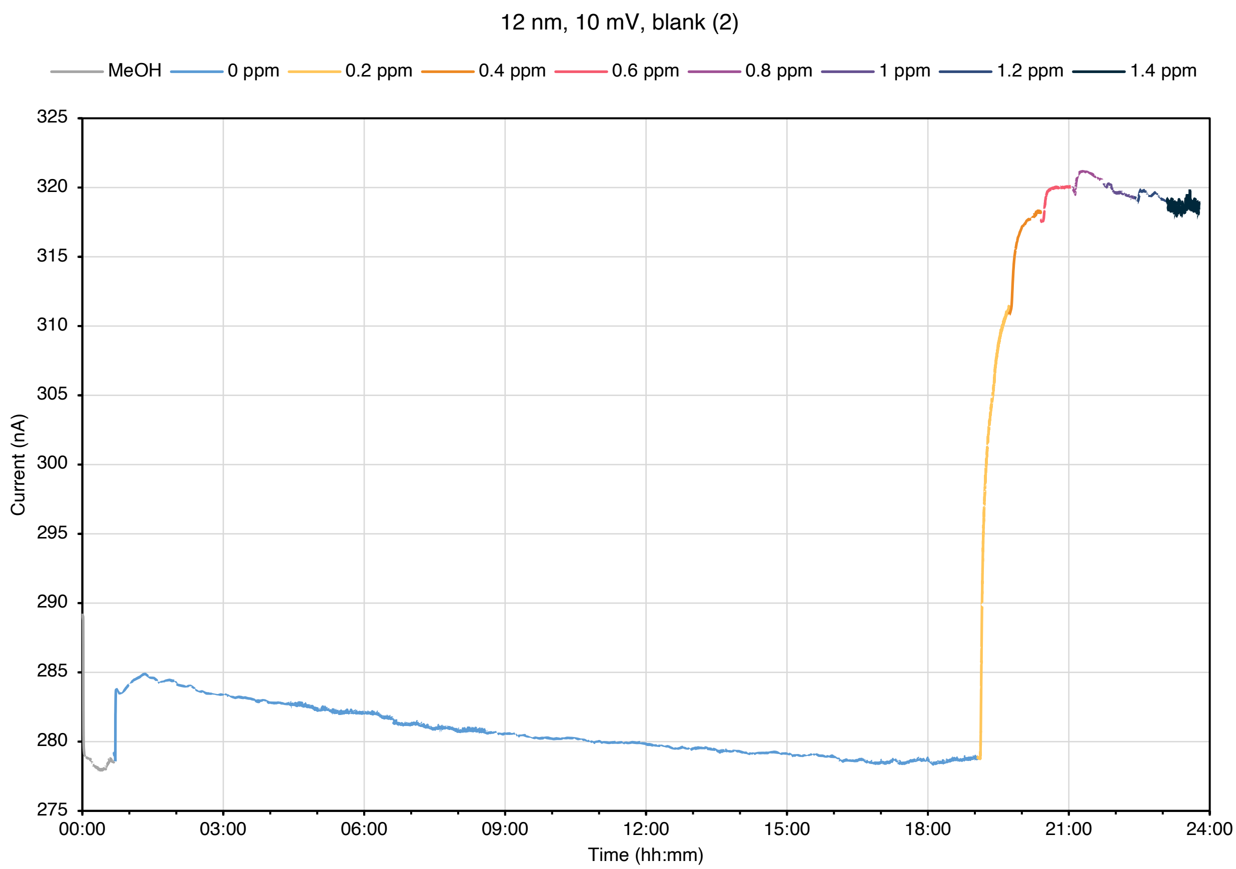


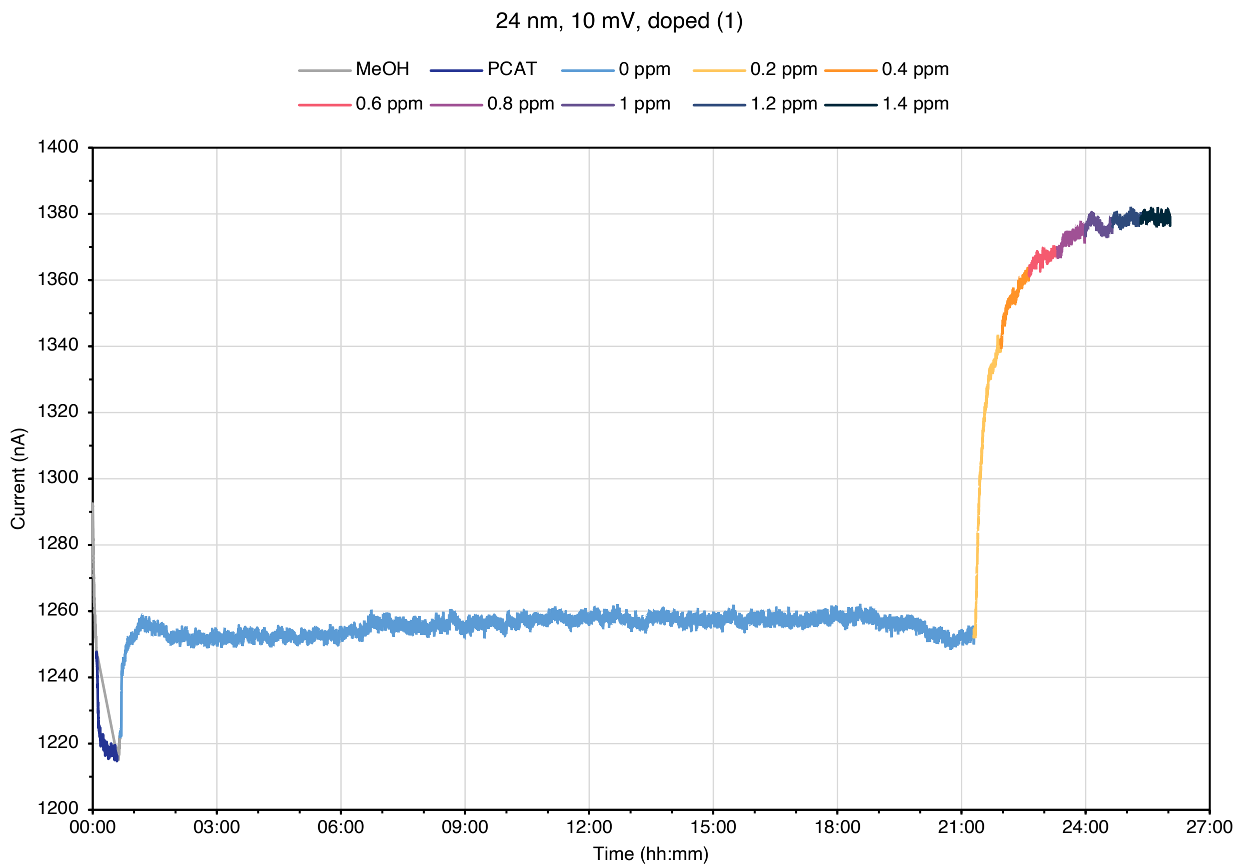
Figure S2. Raw data from the chemiresistive sensing characteristics as a function of GLC film thickness. The data consists of 2 doped sensors and 2 blank sensors for each thickness (i.e. 12, 24, 38, and 46 nm) and each bias (i.e. 10 mV and 100 mV).



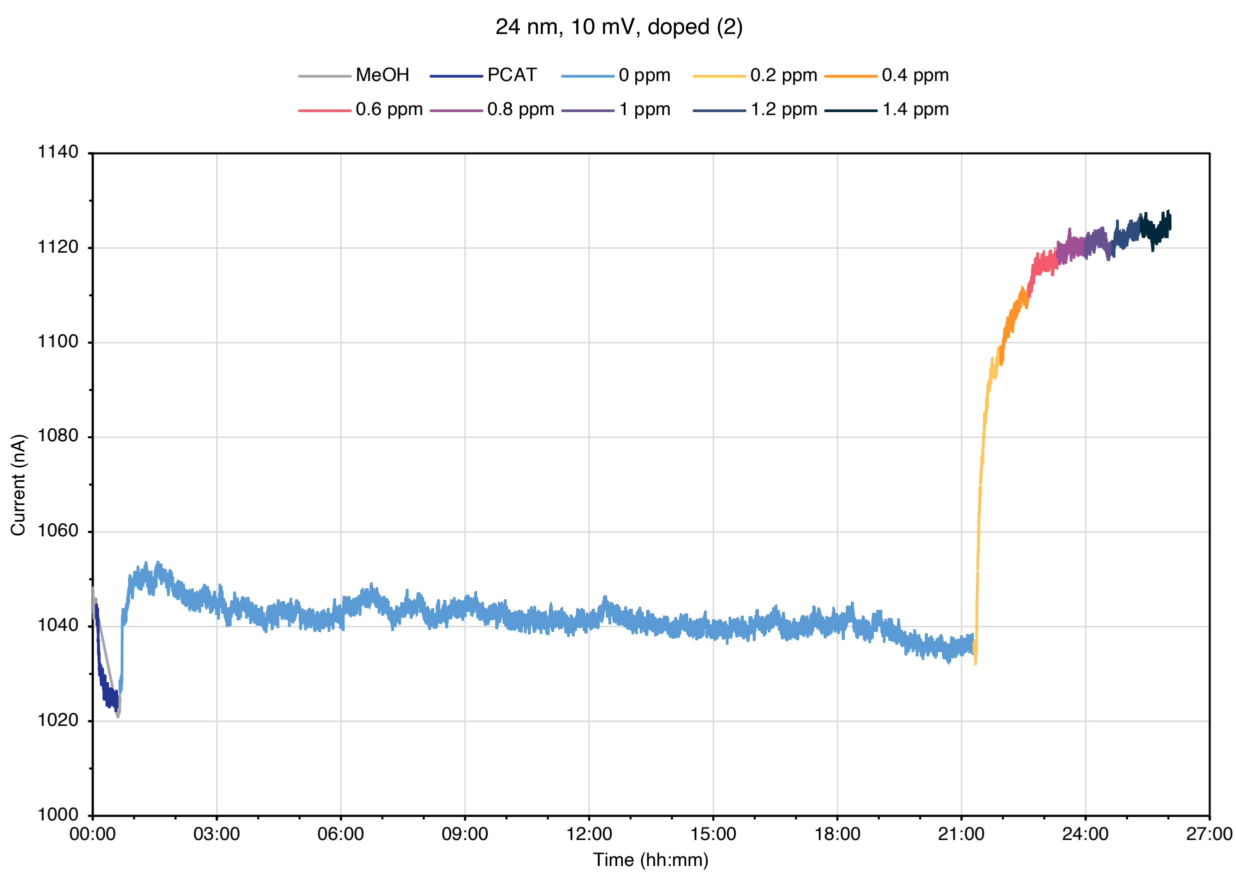



12 nm, 10 mV, blank (1)
MeOH
0 ppm
0.2 ppm
0.4 ppm
0.6 ppm
0.8 ppm
1 ppm
1.2 ppm
1.4 ppm
Current (nA)
360
350
340
330
320
310
300
00:00
03:00
06:00
09:00
12:00
15:00
18:00
21:00
24:00
Time (hh:mm)

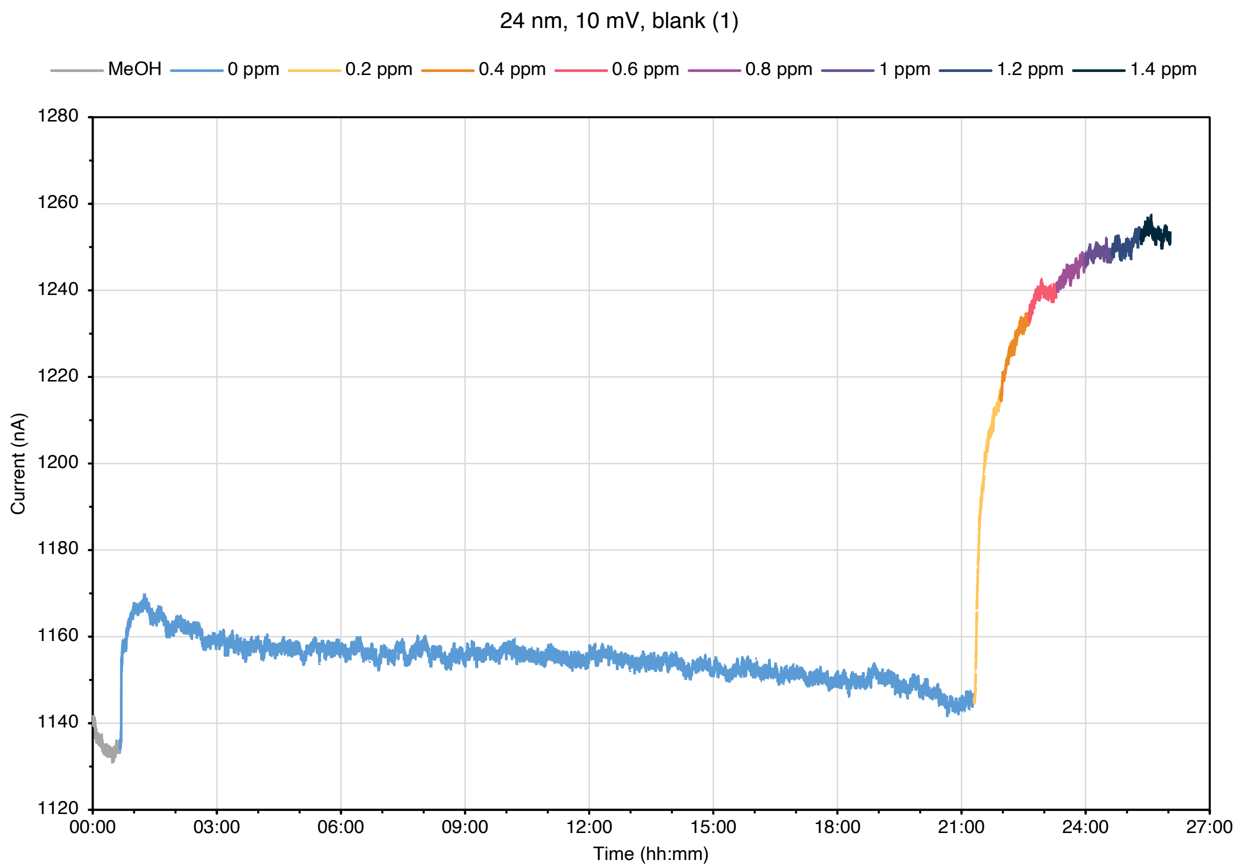

12 nm, 10 mV, blank (2)
MeOH
0 ppm
0.2 ppm
0.4 ppm
0.6 ppm
0.8 ppm
1 ppm
1.2 ppm
1.4 ppm
Current (nA)
325
320
315
310
305
300
295
290
285
280
275
00:00
03:00
06:00
09:00
12:00
15:00
18:00
21:00
24:00
Time (hh:mm)

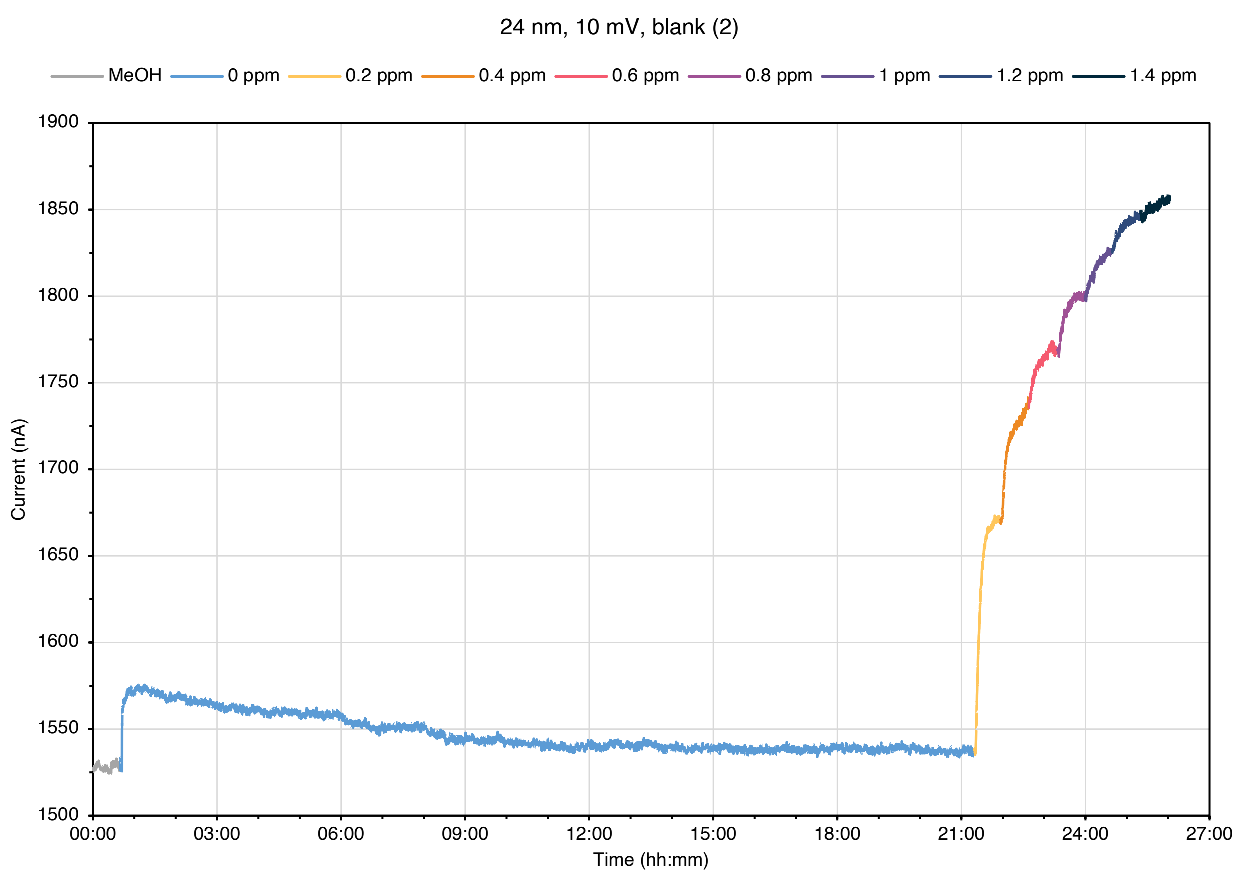


24 nm, 10 mV, doped (1)
MeOH
PCAT
0 ppm
0.2 ppm
0.4 ppm
0.6 ppm
0.8 ppm
1 ppm
1.2 ppm
1.4 ppm
Current (nA)
1400
1380
1360
1340
1320
1300
1280
1260
1240
1220
1200
00:00
03:00
06:00
09:00
12:00
15:00
18:00
21:00
24:00
27:00
Time (hh:mm)

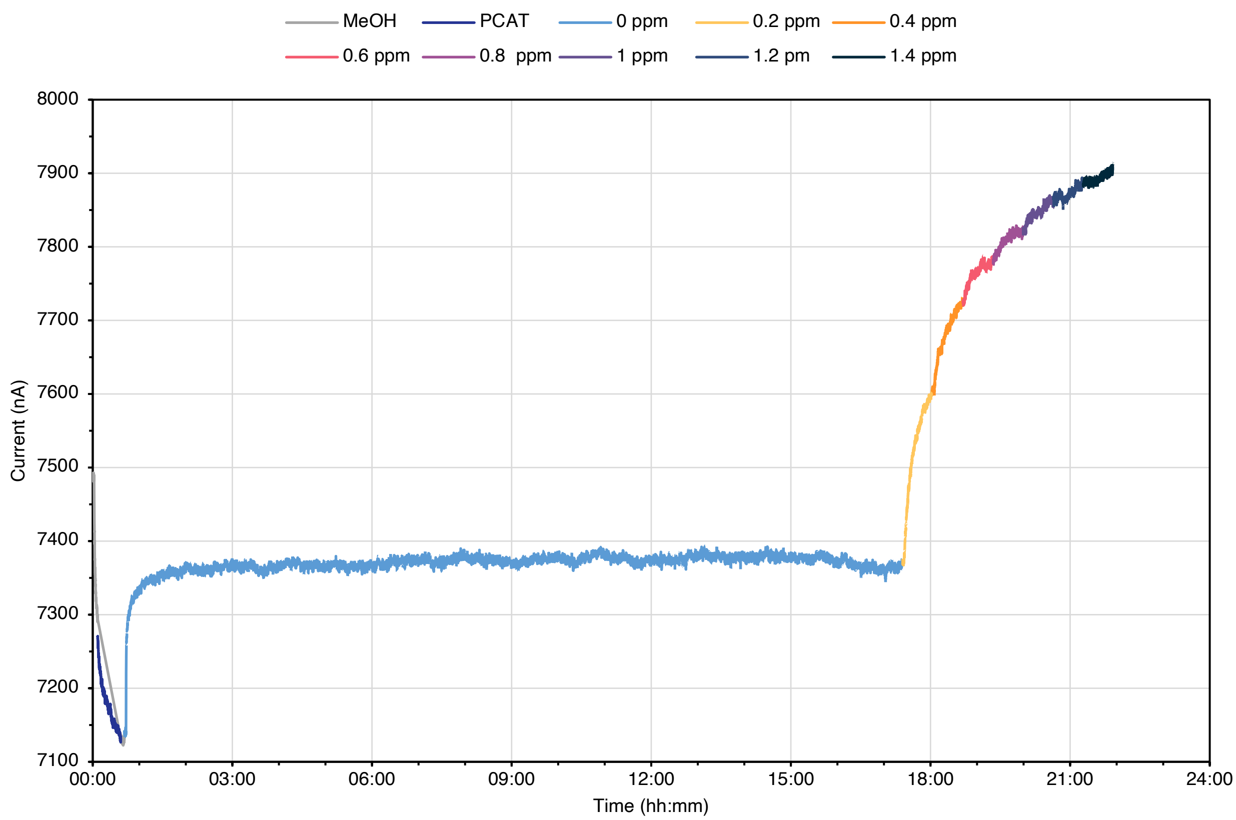


24 nm, 10 mV, doped (2)
MeOH
PCAT
0 ppm
0.2 ppm
0.4 ppm
0.6 ppm
0.8 ppm
1 ppm
1.2 ppm
1.4 ppm
Current (nA)
1140
1120
1100
1080
1060
1040
1020
1000
00:00
03:00
06:00
09:00
12:00
15:00
18:00
21:00
24:00
27:00
Time (hh:mm)

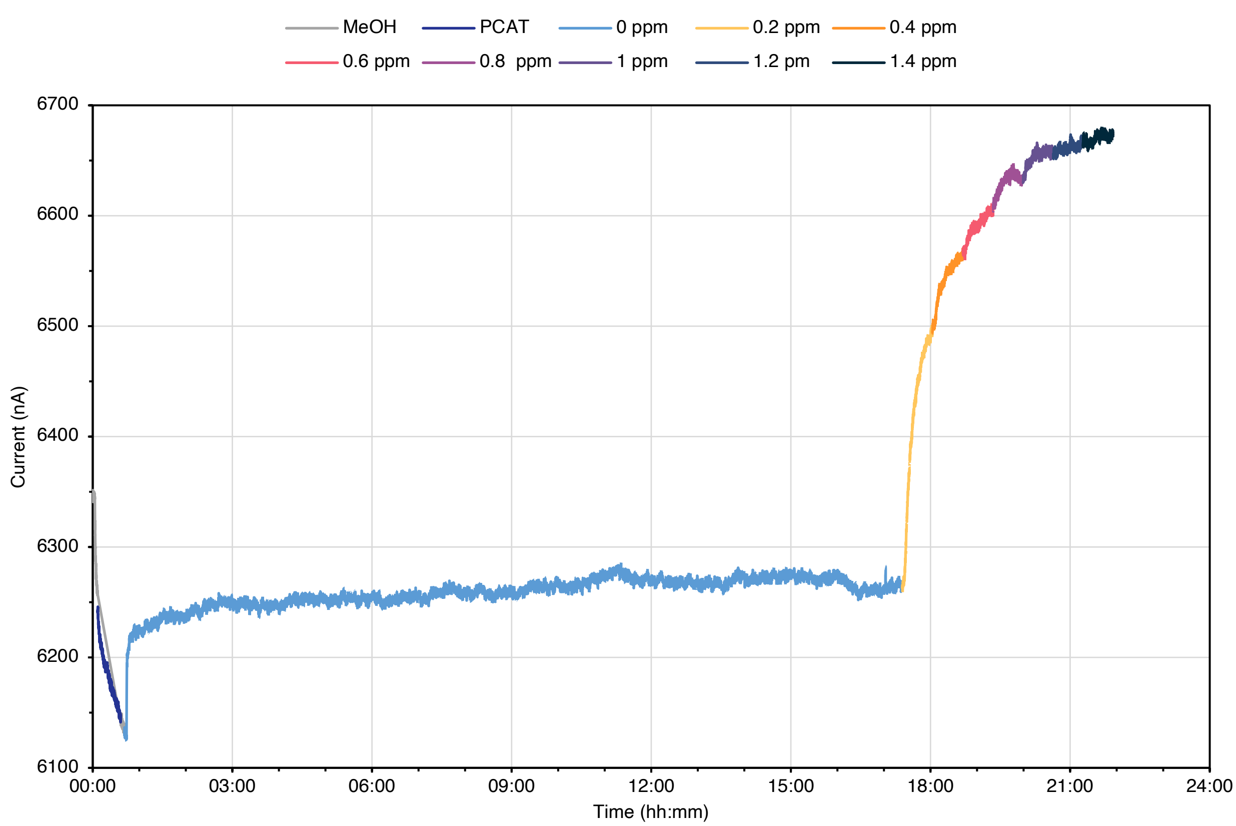

24 nm, 10 mV, blank (1)
MeOH
0 ppm
0.2 ppm
0.4 ppm
0.6 ppm
0.8 ppm
1 ppm
1.2 ppm
1.4 ppm
Current (nA)
1280
1260
1240
1220
1200
1180
1160
1140
1120
00:00
03:00
06:00
09:00
12:00
15:00
18:00
21:00
24:00
27:00
Time (hh:mm)

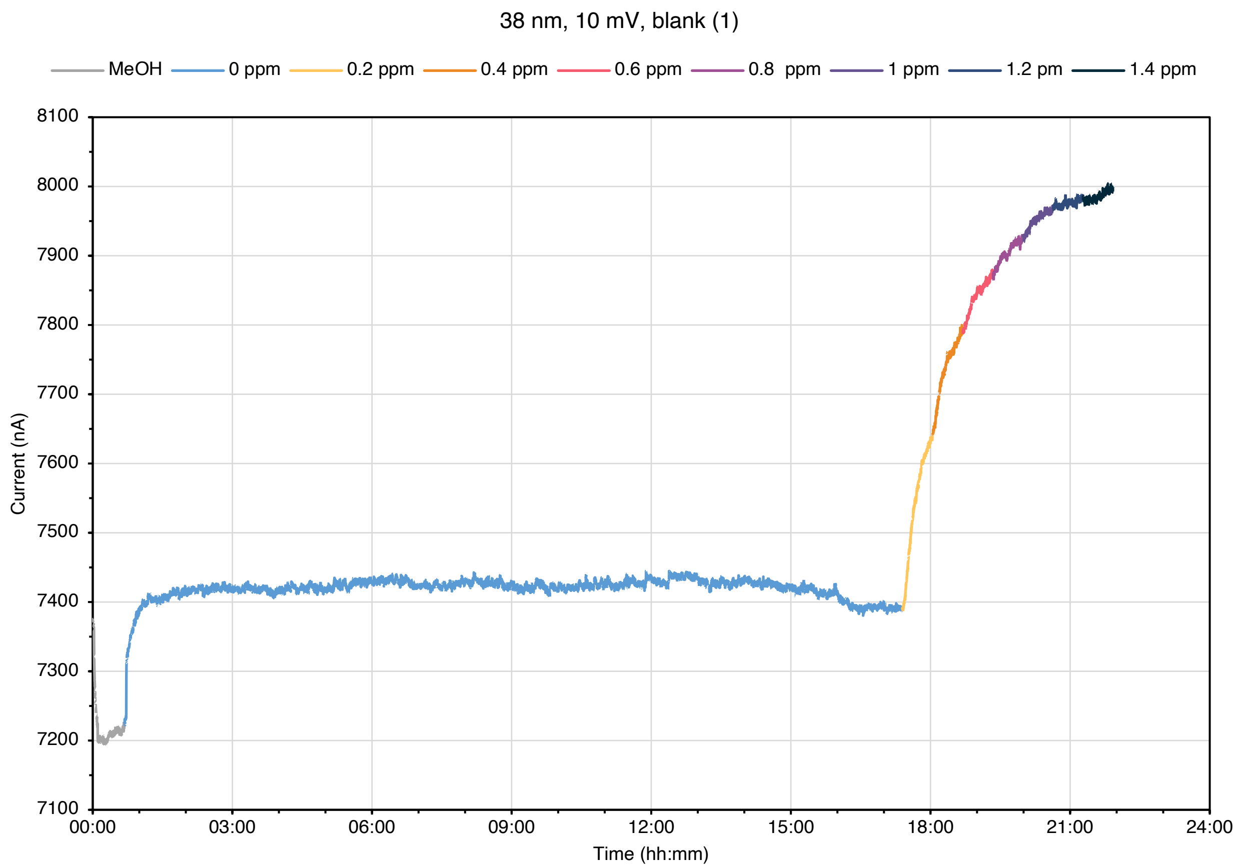

24 nm, 10 mV, blank (2)
MeOH
0 ppm
0.2 ppm
0.4 ppm
0.6 ppm
0.8 ppm
1 ppm
1.2 ppm
1.4 ppm
Current (nA)
1900
1850
1800
1750
1700
1650
1600
1550
1500
00:00
03:00
06:00
09:00
12:00
15:00
18:00
21:00
24:00
27:00
Time (hh:mm)

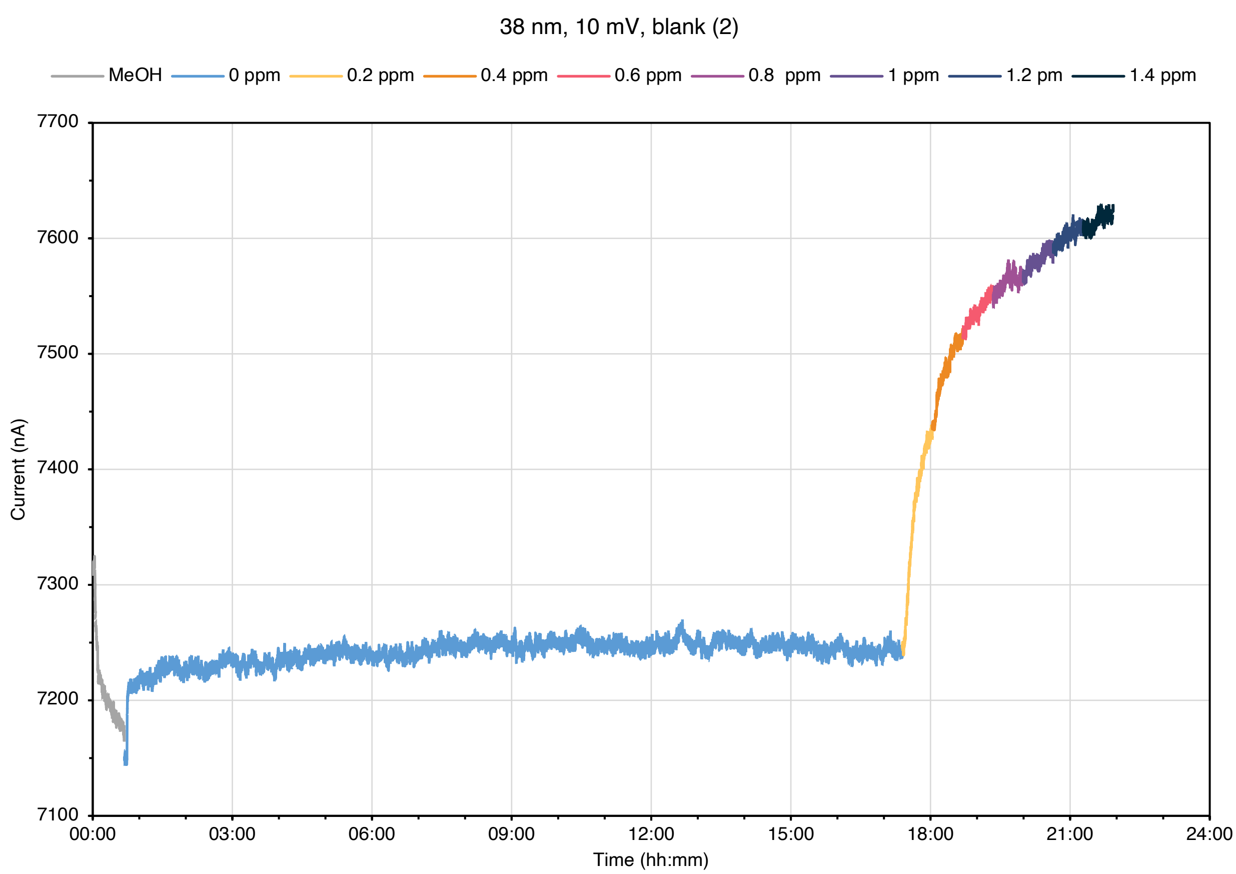
38 nm, 10 mV, doped (1)

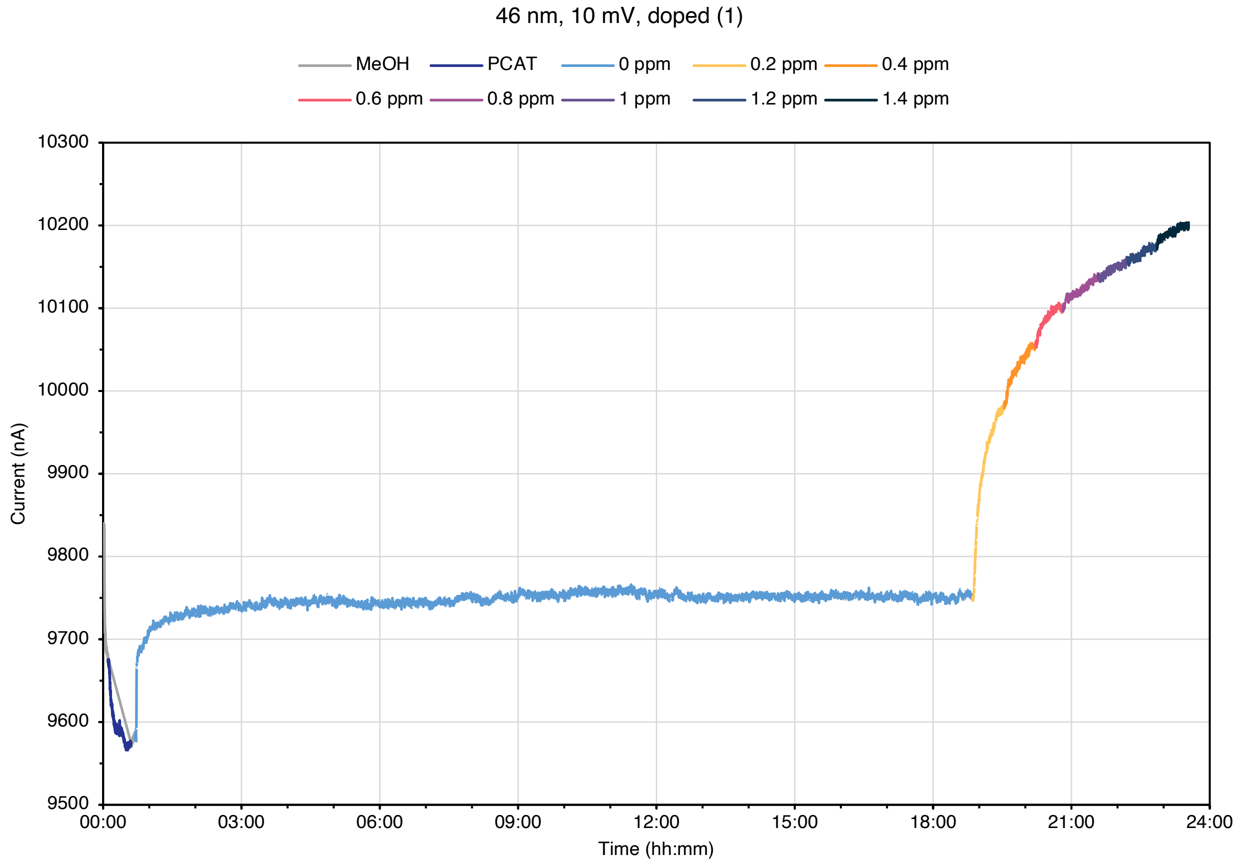


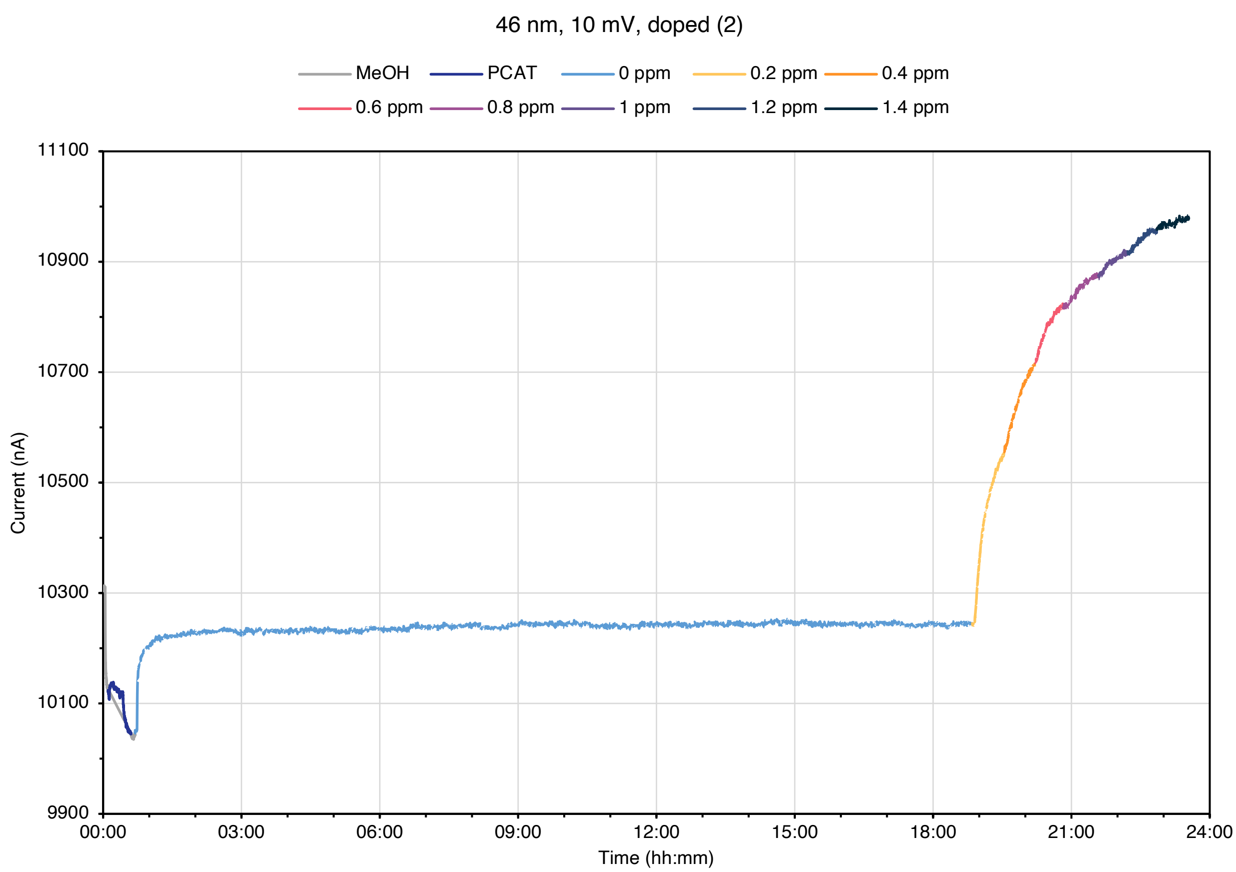
38 nm, 10 mV, doped (2)

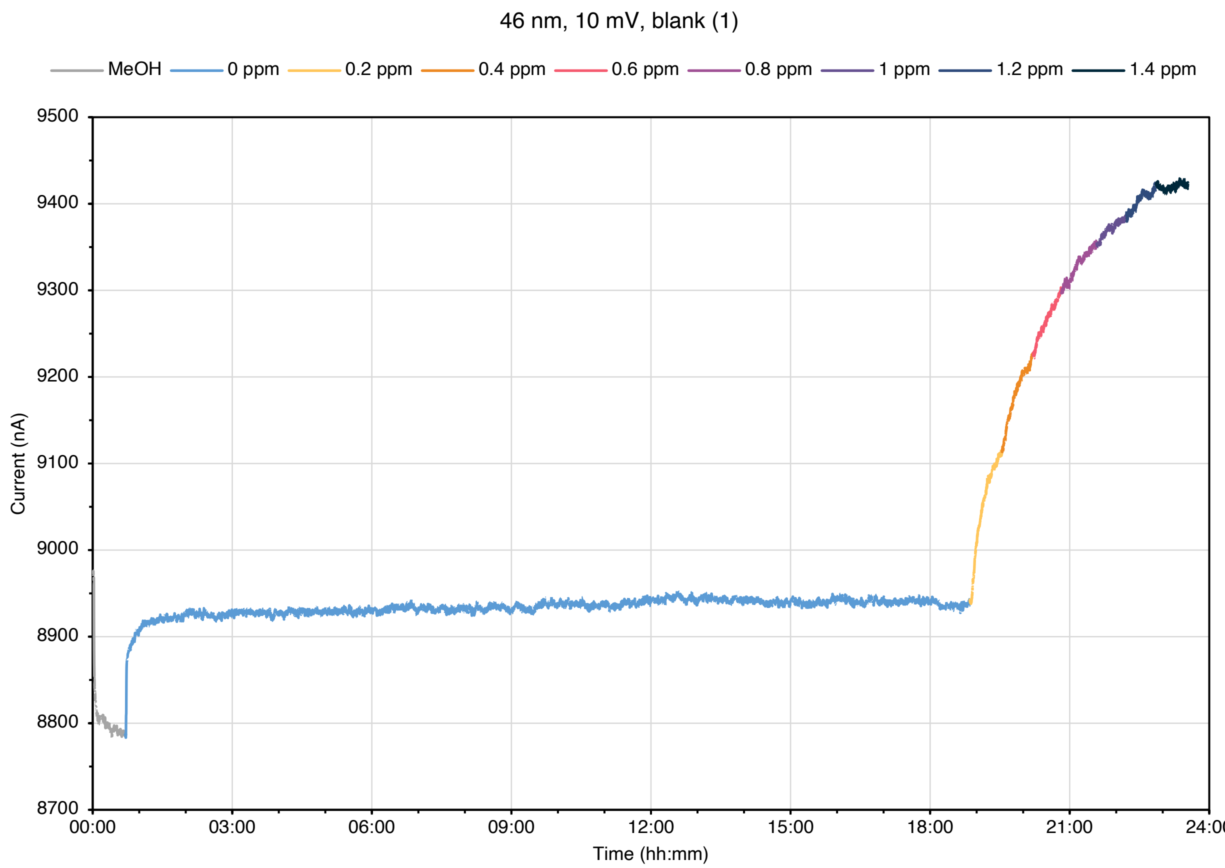


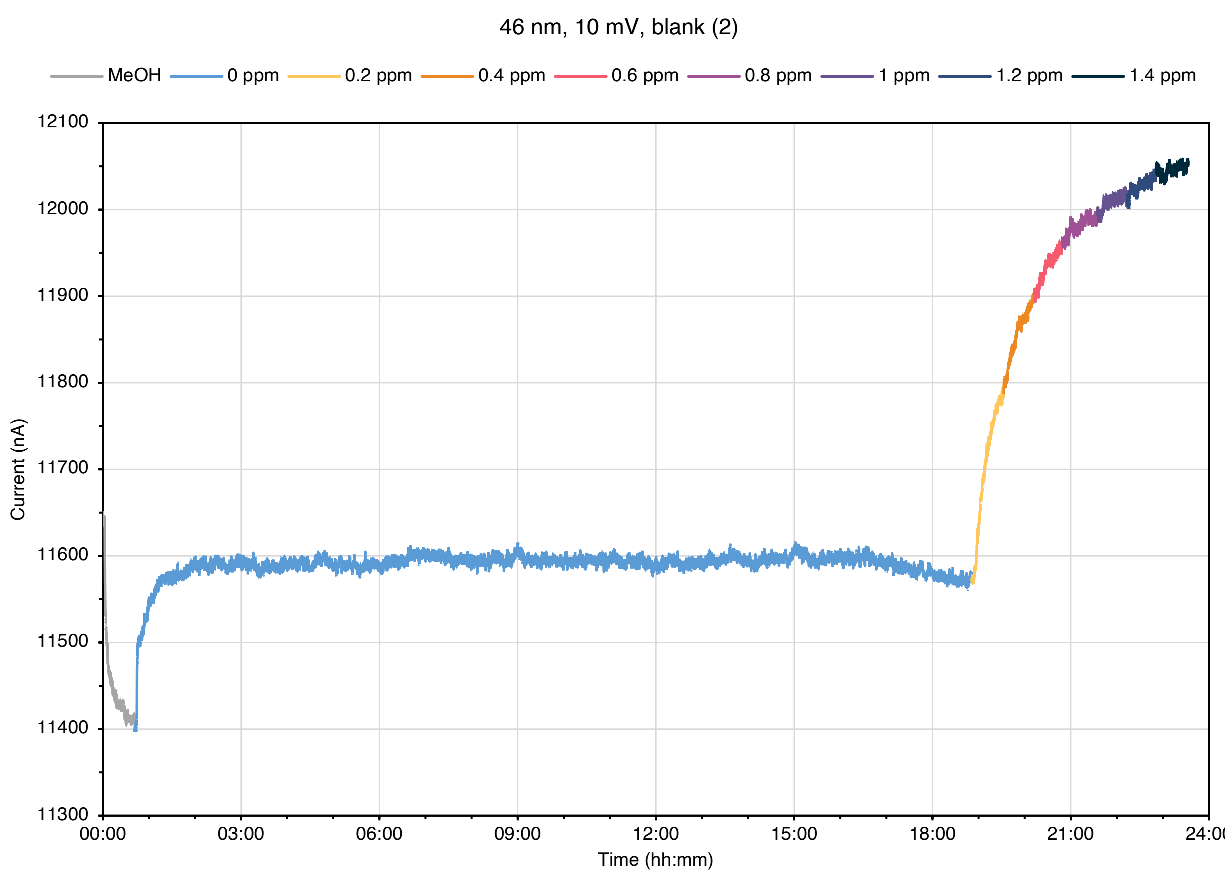

38 nm, 10 mV, blank (1)
MeOH
0 ppm
0.2 ppm
0.4 ppm
0.6 ppm
0.8 ppm
1 ppm
1.2 pm
1.4 ppm
Current (nA)
8100
8000
7900
7800
7700
7600
7500
7400
7300
7200
7100
00:00
03:00
06:00
09:00
12:00
15:00
18:00
21:00
24:00
Time (hh:mm)

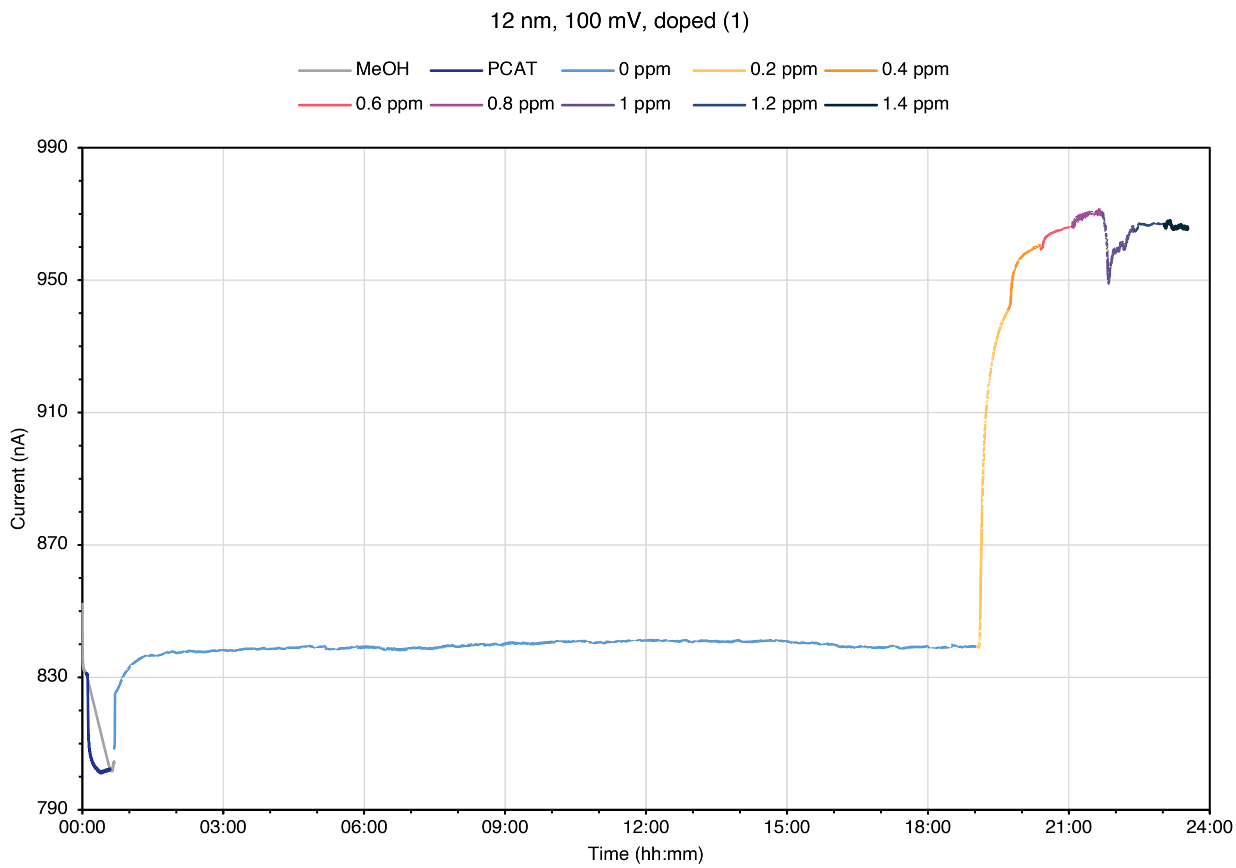

38 nm, 10 mV, blank (2)
MeOH
0 ppm
0.2 ppm
0.4 ppm
0.6 ppm
0.8 ppm
1 ppm
1.2 pm
1.4 ppm
Current (nA)
7700
7600
7500
7400
7300
7200
7100
00:00
03:00
06:00
09:00
12:00
15:00
18:00
21:00
24:00
Time (hh:mm)

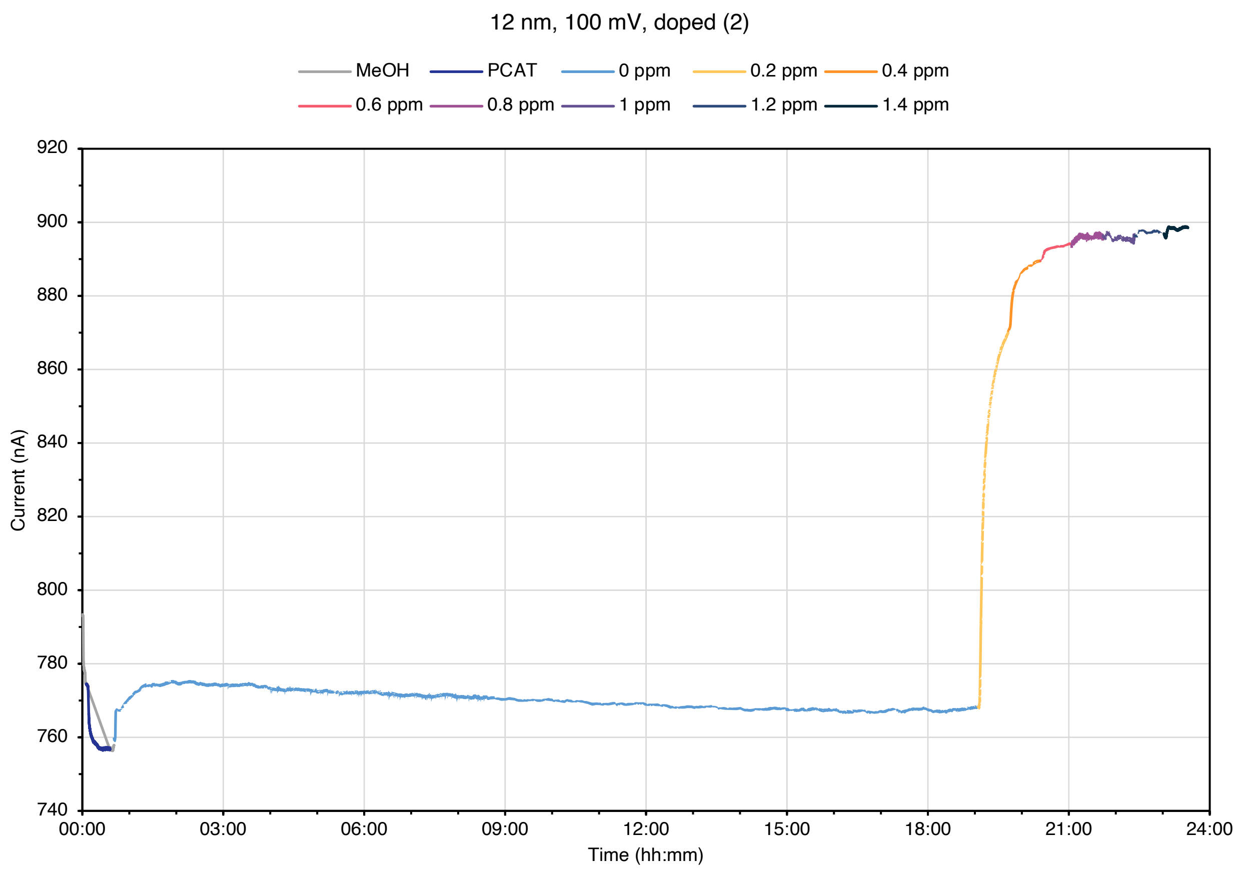

46 nm, 10 mV, doped (1)
MeOH
PCAT
0 ppm
0.2 ppm
0.4 ppm
0.6 ppm
0.8 ppm
1 ppm
1.2 ppm
1.4 ppm
Current (nA)
Time (hh:mm)
10300
10200
10100
10000
9900
9800
9700
9600
9500
00:00
03:00
06:00
09:00
12:00
15:00
18:00
21:00
24:00

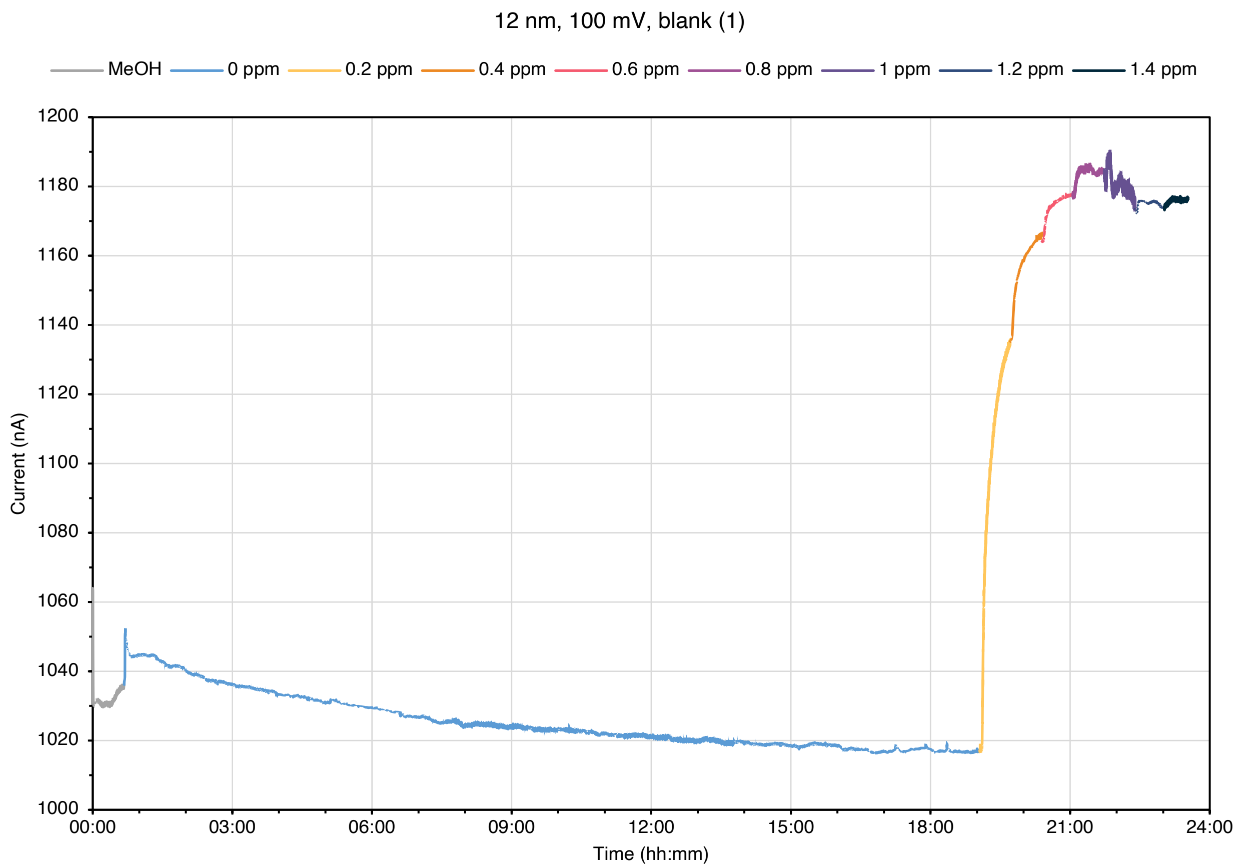

46 nm, 10 mV, doped (2)
MeOH
PCAT
0 ppm
0.2 ppm
0.4 ppm
0.6 ppm
0.8 ppm
1 ppm
1.2 ppm
1.4 ppm
Current (nA)
Time (hh:mm)
11100
10900
10700
10500
10300
10100
9900
00:00
03:00
06:00
09:00
12:00
15:00
18:00
21:00
24:00


46 nm, 10 mV, blank (1)
MeOH
0 ppm
0.2 ppm
0.4 ppm
0.6 ppm
0.8 ppm
1 ppm
1.2 ppm
1.4 ppm
Current (nA)
9500
9400
9300
9200
9100
9000
8900
8800
8700
00:00
03:00
06:00
09:00
12:00
15:00
18:00
21:00
24:00
Time (hh:mm)

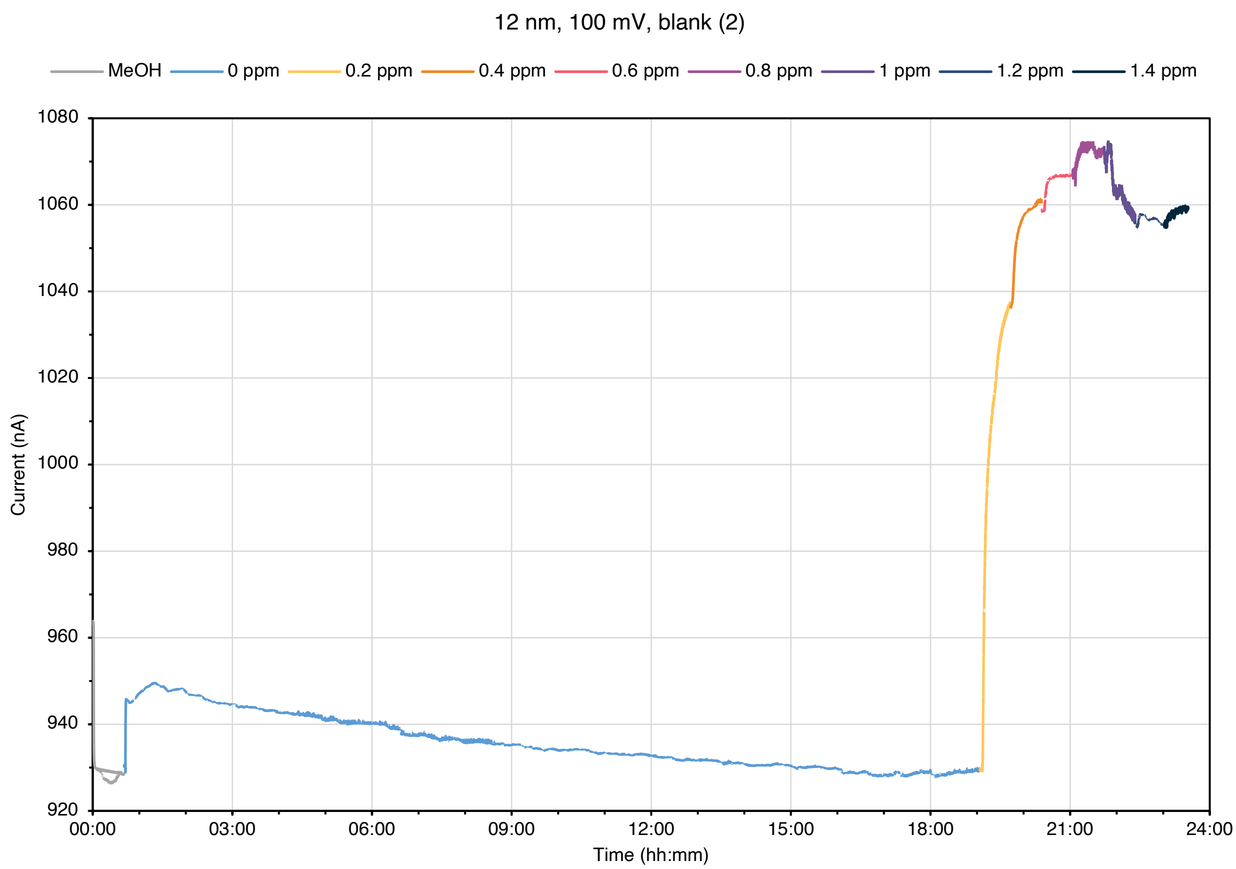

46 nm, 10 mV, blank (2)
MeOH
0 ppm
0.2 ppm
0.4 ppm
0.6 ppm
0.8 ppm
1 ppm
1.2 ppm
1.4 ppm
Current (nA)
12100
12000
11900
11800
11700
11600
11500
11400
11300
00:00
03:00
06:00
09:00
12:00
15:00
18:00
21:00
24:00
Time (hh:mm)


12 nm, 100 mV, doped (1)
MeOH
PCAT
0 ppm
0.2 ppm
0.4 ppm
0.6 ppm
0.8 ppm
1 ppm
1.2 ppm
1.4 ppm
Current (nA)
990
950
910
870
830
790
00:00
03:00
06:00
09:00
12:00
15:00
18:00
21:00
24:00
Time (hh:mm)

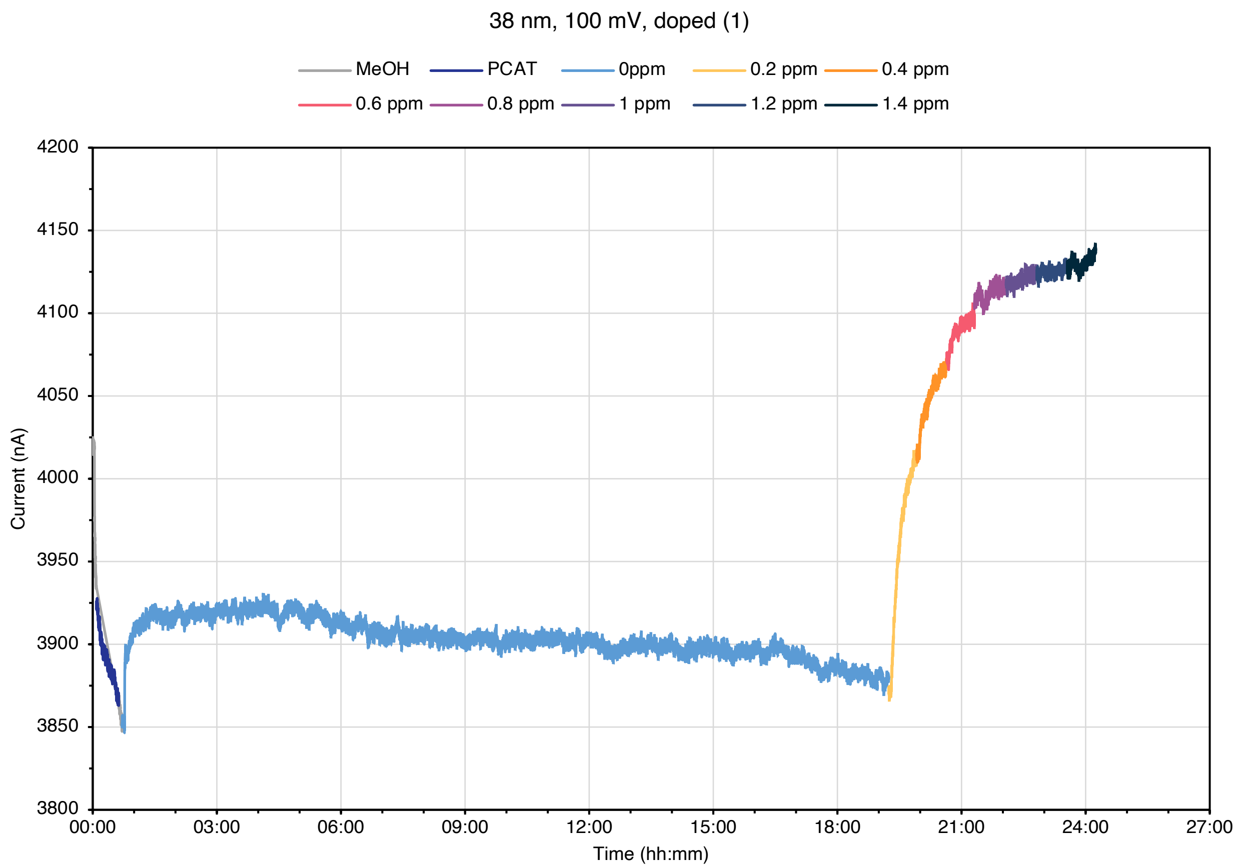

12 nm, 100 mV, doped (2)
MeOH
PCAT
0 ppm
0.2 ppm
0.4 ppm
0.6 ppm
0.8 ppm
1 ppm
1.2 ppm
1.4 ppm
Current (nA)
920
900
880
860
840
820
800
780
760
740
00:00
03:00
06:00
09:00
12:00
15:00
18:00
21:00
24:00
Time (hh:mm)

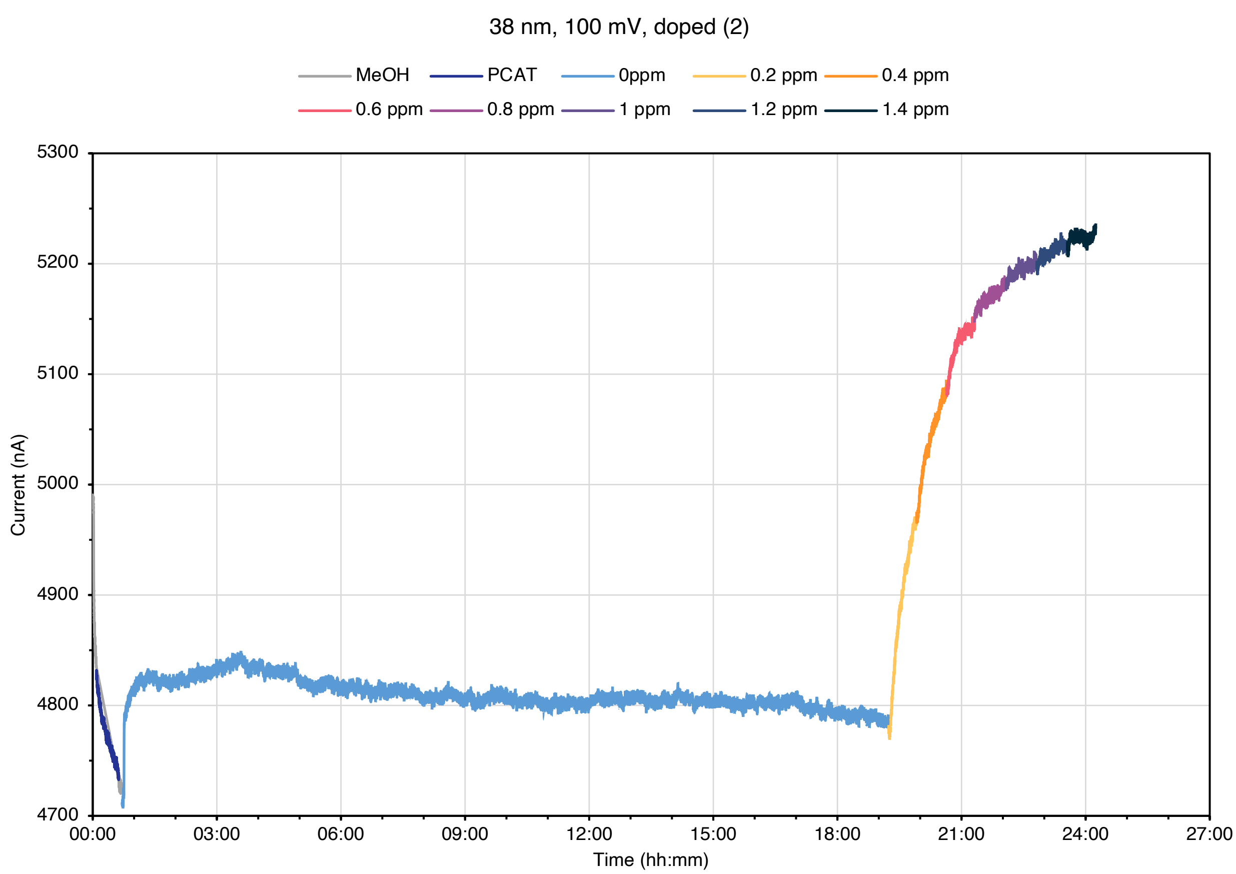


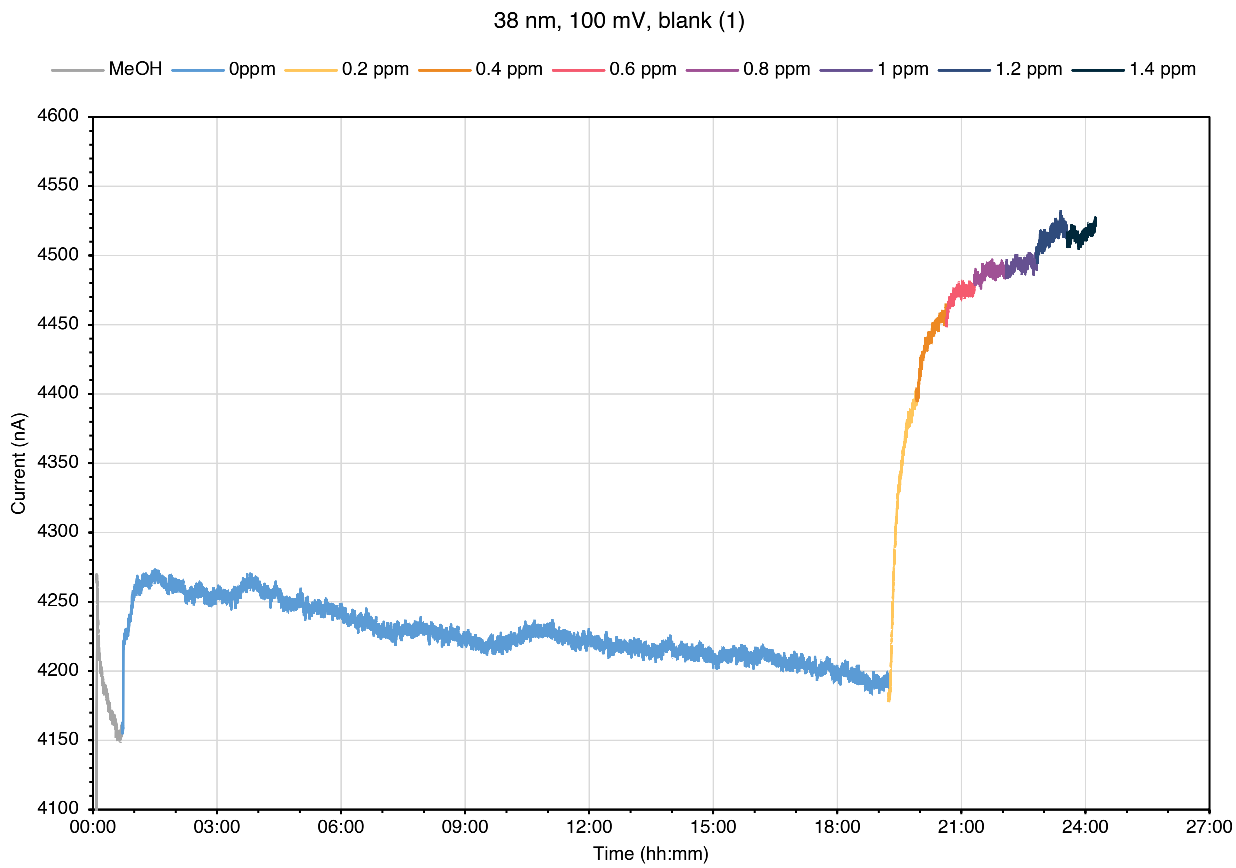
12 nm, 100 mV, blank (1)
MeOH
0 ppm
0.2 ppm
0.4 ppm
0.6 ppm
0.8 ppm
1 ppm
1.2 ppm
1.4 ppm
Current (nA)
1200
1180
1160
1140
1120
1100
1080
1060
1040
1020
1000
00:00
03:00
06:00
09:00
12:00
15:00
18:00
21:00
24:00
Time (hh:mm)

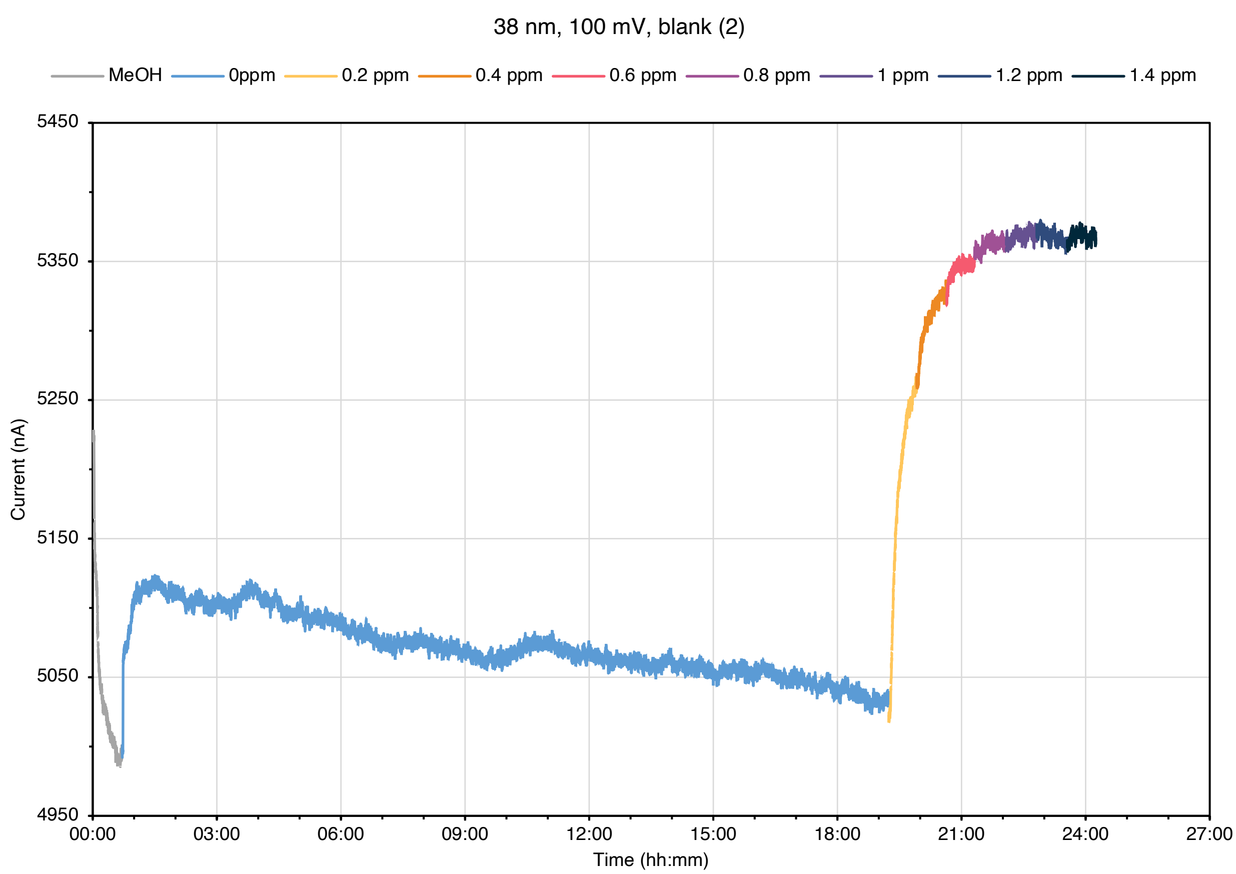


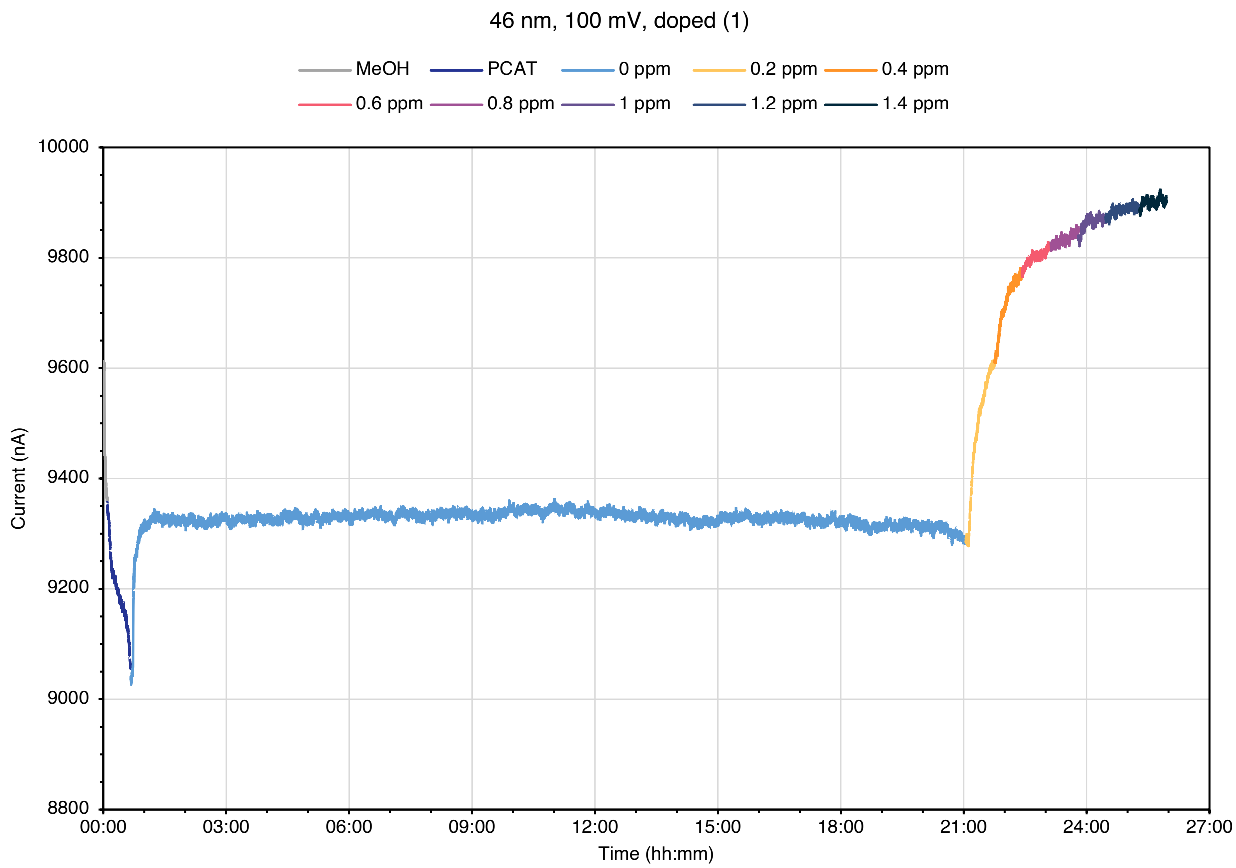
12 nm, 100 mV, blank (2)
MeOH
0 ppm
0.2 ppm
0.4 ppm
0.6 ppm
0.8 ppm
1 ppm
1.2 ppm
1.4 ppm
Current (nA)
1080
1060
1040
1020
1000
980
960
940
920
00:00
03:00
06:00
09:00
12:00
15:00
18:00
21:00
24:00
Time (hh:mm)

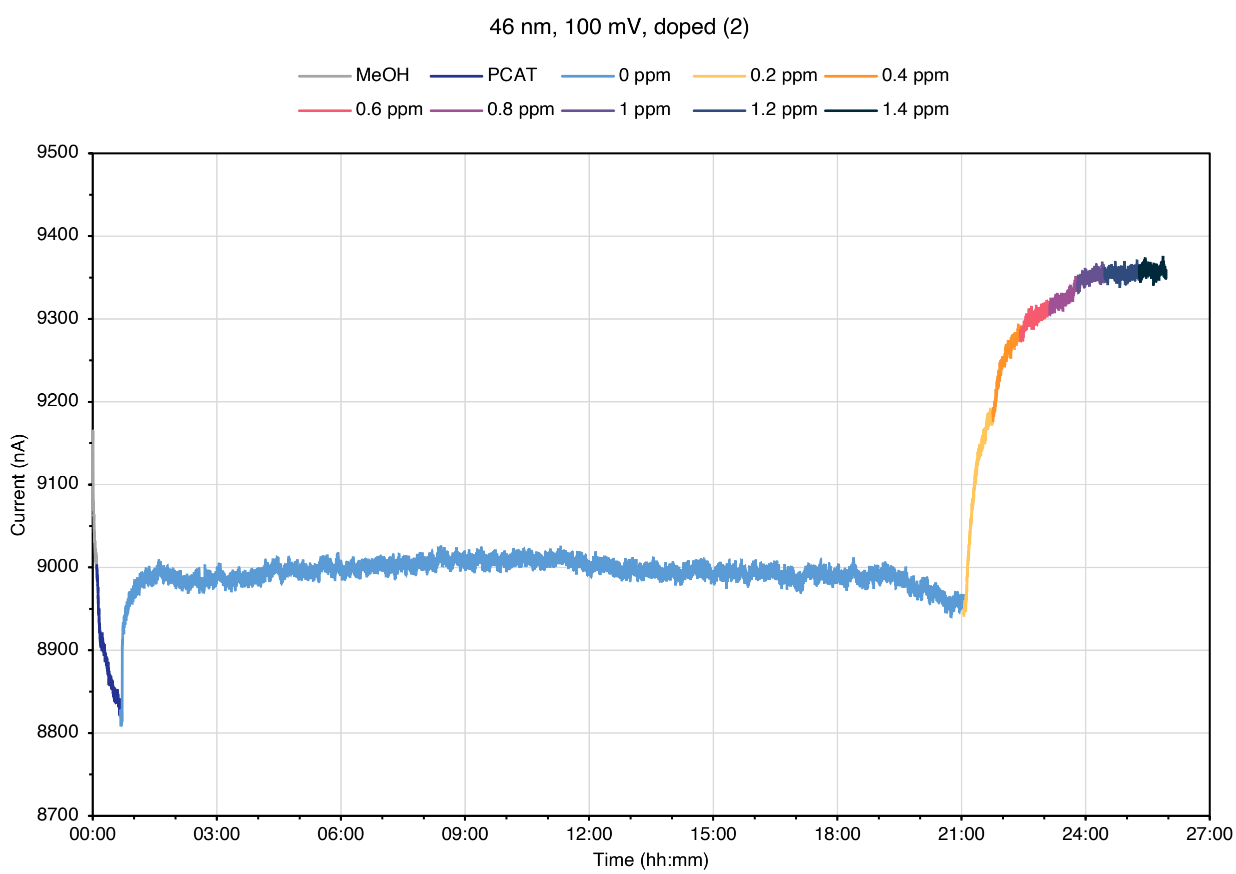

38 nm, 100 mV, doped (1)
MeOH
PCAT
0ppm
0.2 ppm
0.4 ppm
0.6 ppm
0.8 ppm
1 ppm
1.2 ppm
1.4 ppm
Current (nA)
4200
4150
4100
4050
4000
3950
3900
3850
3800
00:00
03:00
06:00
09:00
12:00
15:00
18:00
21:00
24:00
27:00
Time (hh:mm)


38 nm, 100 mV, doped (2)
MeOH
PCAT
0ppm
0.2 ppm
0.4 ppm
0.6 ppm
0.8 ppm
1 ppm
1.2 ppm
1.4 ppm
Current (nA)
5300
5200
5100
5000
4900
4800
4700
00:00
03:00
06:00
09:00
12:00
15:00
18:00
21:00
24:00
27:00
Time (hh:mm)


38 nm, 100 mV, blank (1)
MeOH
0ppm
0.2 ppm
0.4 ppm
0.6 ppm
0.8 ppm
1 ppm
1.2 ppm
1.4 ppm
Current (nA)
4600
4550
4500
4450
4400
4350
4300
4250
4200
4150
4100
00:00
03:00
06:00
09:00
12:00
15:00
18:00
21:00
24:00
27:00
Time (hh:mm)


38 nm, 100 mV, blank (2)
MeOH
0ppm
0.2 ppm
0.4 ppm
0.6 ppm
0.8 ppm
1 ppm
1.2 ppm
1.4 ppm
Current (nA)
5450
5350
5250
5150
5050
4950
00:00
03:00
06:00
09:00
12:00
15:00
18:00
21:00
24:00
27:00
Time (hh:mm)


46 nm, 100 mV, doped (1)
MeOH
PCAT
0 ppm
0.2 ppm
0.4 ppm
0.6 ppm
0.8 ppm
1 ppm
1.2 ppm
1.4 ppm
Current (nA)
10000
9800
9600
9400
9200
9000
8800
00:00
03:00
06:00
09:00
12:00
15:00
18:00
21:00
24:00
27:00
Time (hh:mm)


46 nm, 100 mV, doped (2)
MeOH
PCAT
0 ppm
0.2 ppm
0.4 ppm
0.6 ppm
0.8 ppm
1 ppm
1.2 ppm
1.4 ppm
Current (nA)
9500
9400
9300
9200
9100
9000
8900
8800
8700
00:00
03:00
06:00
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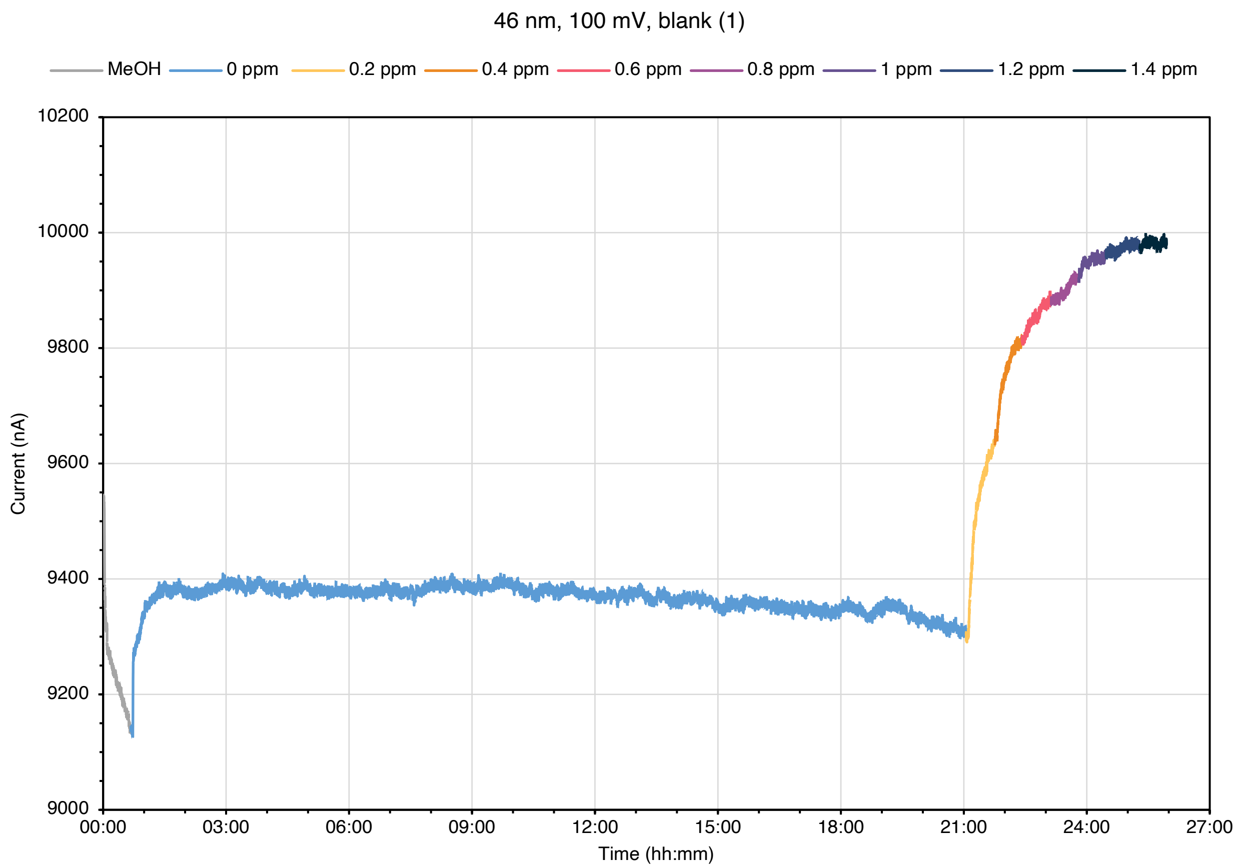
15:00
18:00
21:00
24:00
27:00
Time (hh:mm)


46 nm, 100 mV, blank (1)
MeOH
0 ppm
0.2 ppm
0.4 ppm
0.6 ppm
0.8 ppm
1 ppm
1.2 ppm
1.4 ppm
Current (nA)
10200
10000
9800
9600
9400
9200
9000
00:00
03:00
06:00
09:00
12:00
15:00
18:00
21:00
24:00
27:00
Time (hh:mm)

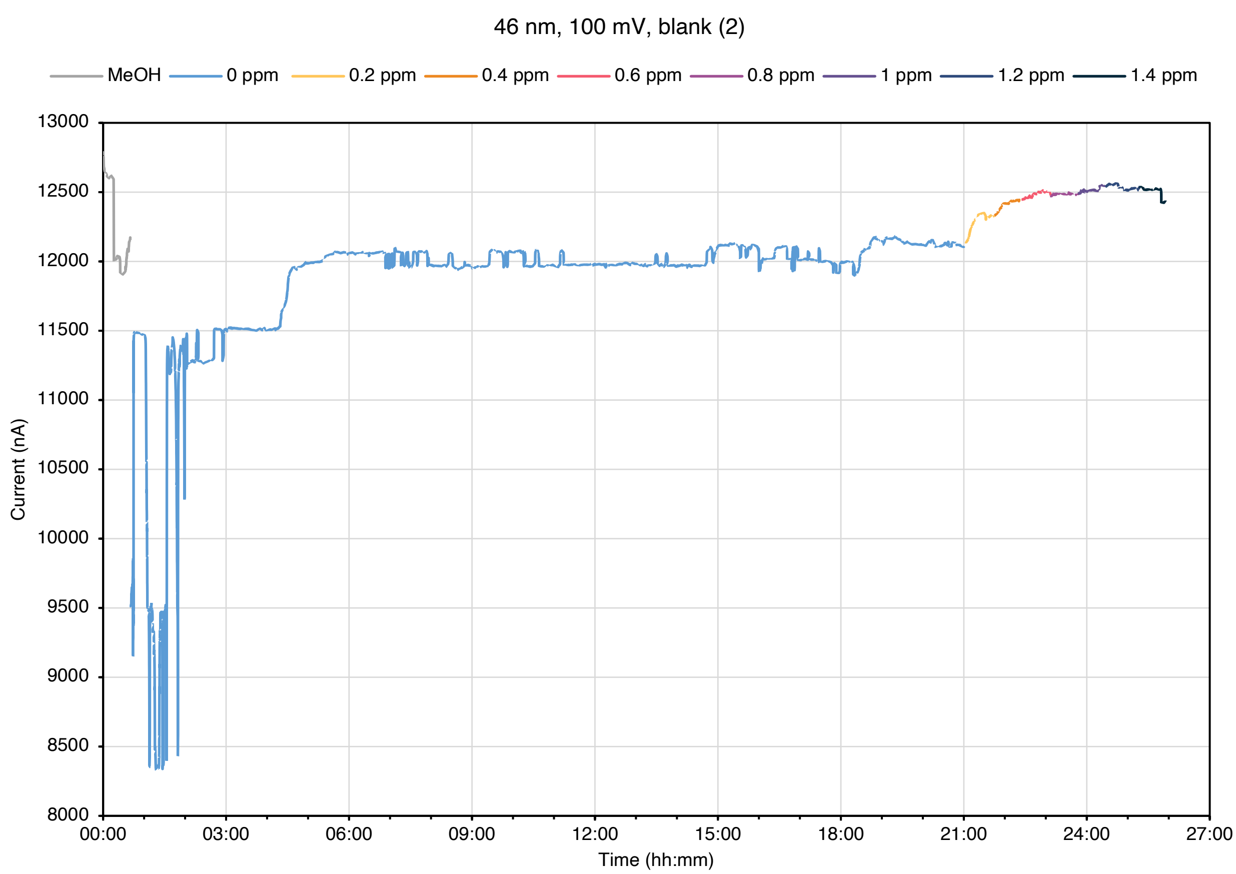

46 nm, 100 mV, blank (2)
MeOH
0 ppm
0.2 ppm
0.4 ppm
0.6 ppm
0.8 ppm
1 ppm
1.2 ppm
1.4 ppm
Current (nA)
13000
12500
12000
11500
11000
10500
10000
9500
9000
8500
8000
00:00
03:00
06:00
09:00
12:00
15:00
18:00
21:00
24:00
27:00
Time (hh:mm)

Table S1. Equations of the models used to fit the data in **Figure S2**, as well as the curve parameters obtained with each of the sensors.

Langmuir adsorption isotherm: $y = \frac{ABx}{1+Bx}$

Exponential decay: $y = i(1 - e^{-jx})$

Freundlich adsorption isotherm: $y = mx^{1/n}$

Doped sensors

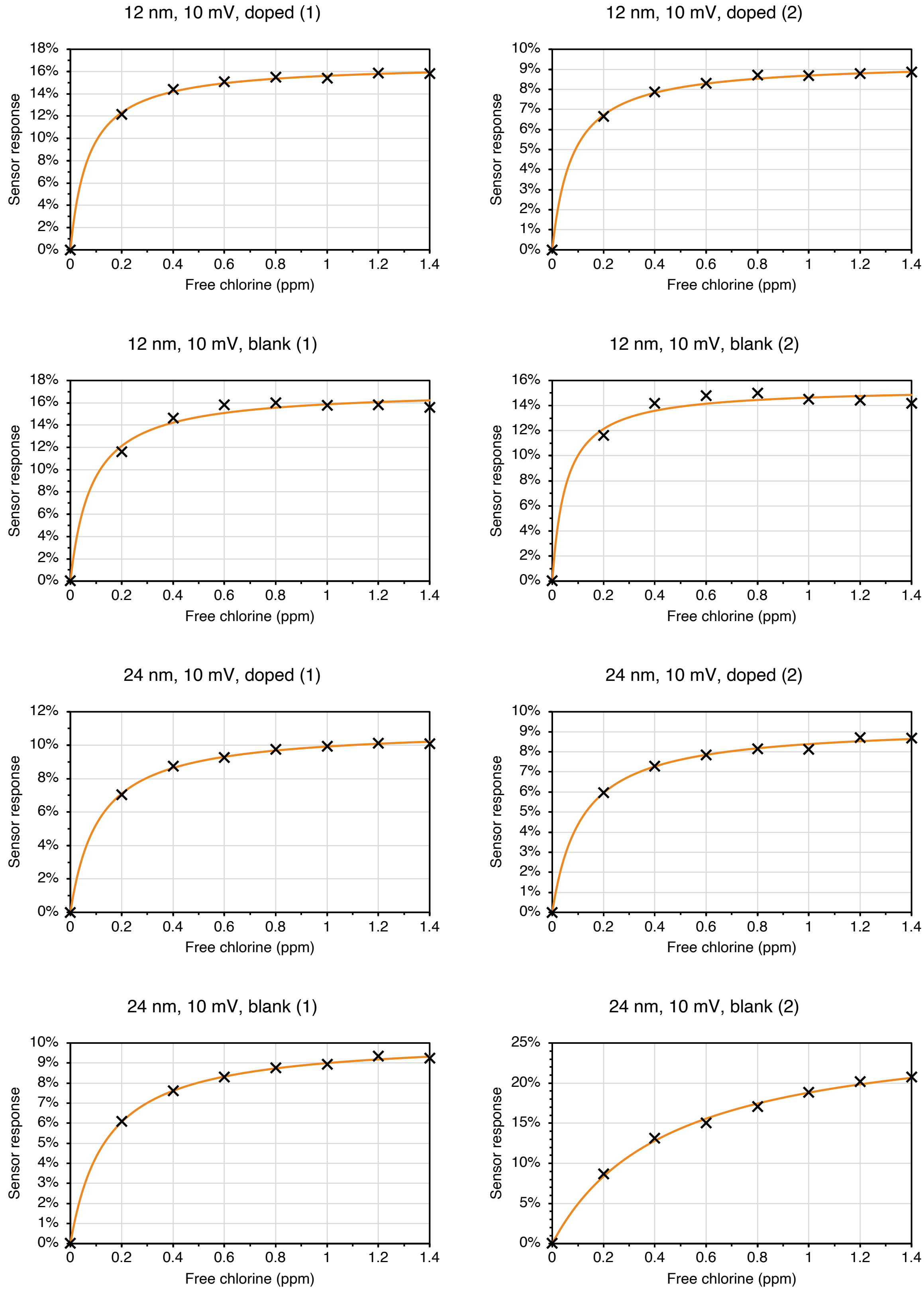
	Langmuir			Exponential			Freundlich		
	A	B	R^2	i	j	R^2	m	n	R^2
10 mV									
12 nm	0.1678	13.7553	0.9991	0.1556	7.3097	0.9980	0.1516	10.4393	0.9894
12 nm	0.0943	12.2518	0.9994	0.0868	6.8688	0.9967	0.0869	7.3615	0.9948
24 nm	0.1101	9.0850	0.9995	0.0992	5.7888	0.9966	0.0987	5.8172	0.9932
24 nm	0.0934	8.7750	0.9981	0.0838	5.7196	0.9917	0.0835	5.5675	0.9951
38 nm	0.0915	2.6758	0.9993	0.0724	2.6500	0.9963	0.0657	2.6099	0.9919
38 nm	0.0754	4.5298	0.9988	0.0637	3.7066	0.9910	0.0612	3.5431	0.9960
46 nm	0.0535	3.6201	0.9972	0.0441	3.1880	0.9875	0.0414	3.0805	0.9983
46 nm	0.0931	2.4328	0.9998	0.0727	2.4905	0.9981	0.0650	2.4879	0.9911
100 mV									
12 nm	0.1612	17.2411	0.9949	0.1517	7.9730	0.9987	0.1516	10.4396	0.9874
12 nm	0.1783	15.8516	0.9985	0.1669	7.8144	0.9994	0.1671	9.3111	0.9930
38 nm	0.0788	3.9558	0.9991	0.0654	3.4401	0.9981	0.0622	3.2825	0.9879
38 nm	0.1203	2.5774	0.9966	0.0943	2.6263	0.9993	0.0854	2.5631	0.9801
46 nm	0.0770	4.4994	0.9973	0.0648	3.7705	0.9977	0.0623	3.5559	0.9839
46 nm	0.0520	5.0905	0.9945	0.0444	4.0623	0.9989	0.0430	3.9017	0.9770

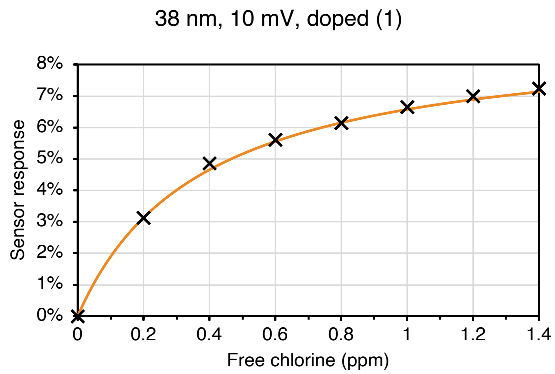
Blank sensors

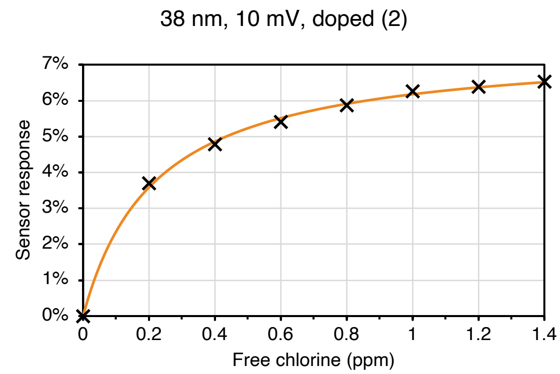
	Langmuir			Exponential			Freundlich		
	A	B	R^2	i	j	R^2	m	n	R^2
10 mV									
12 nm	0.1720	11.9299	0.9924	0.1585	6.5844	0.9990	0.1576	7.6494	0.9799
12 nm	0.1544	18.3155	0.9896	0.1461	8.0345	0.9973	0.1455	11.6104	0.9798
24 nm	0.1024	7.2660	0.9994	0.0905	5.0544	0.9937	0.0894	4.8867	0.9945
24 nm	0.2735	2.2057	0.9980	0.2115	2.2973	0.9931	0.1541	0.0000	#DIV/0!
38 nm	0.1084	2.4534	0.9977	0.0846	2.5263	0.9996	0.0759	2.5028	0.9829
38 nm	0.0609	3.8946	0.9980	0.0505	3.4058	0.9930	0.0479	3.2239	0.9916
46 nm	0.0778	1.7693	0.9984	0.0579	2.0198	0.9996	0.0489	2.1297	0.9868
46 nm	0.0515	2.8837	0.9993	0.0411	2.7989	0.9979	0.0377	2.7218	0.9891

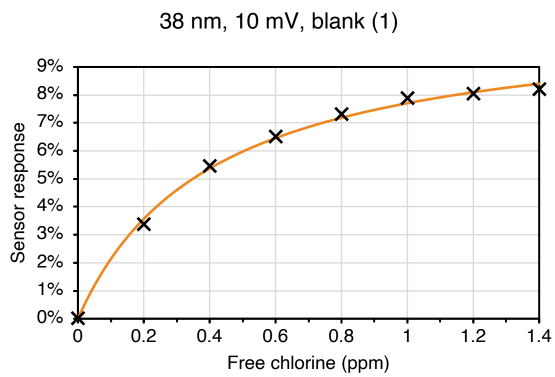
100 mV									
12 nm	0.1715	12.1452	0.9877	0.1583	6.6069	0.9960	0.1572	7.8573	0.9741
12 nm	0.1495	23.0048	0.9741	0.1432	8.6211	0.9845	0.1422	15.6823	0.9643
38 nm	0.0852	6.5103	0.9973	0.0745	4.7763	0.9894	0.0734	4.4752	0.9945
38 nm	0.0729	8.6910	0.9962	0.0656	5.5911	0.9991	0.0649	5.7617	0.9841
46 nm	0.0881	3.6779	0.9971	0.0725	3.3051	0.9991	0.0684	3.1457	0.9814
46 nm	0.0379	6.2814	0.9307	0.0332	4.5225	0.9495	0.0323	4.7866	0.8995

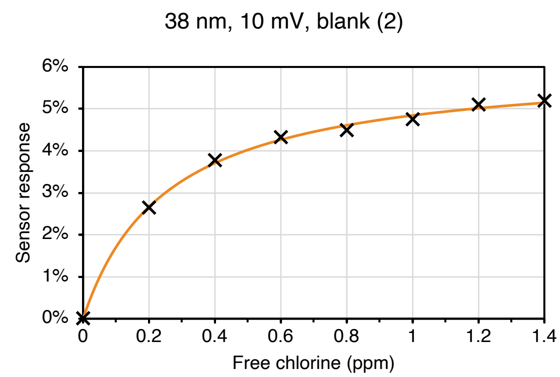
Figure S3. Calibration curves obtained with the raw data in **Figure S2**, fitted to a Langmuir adsorption isotherm using the curve parameters in **Table S1**.

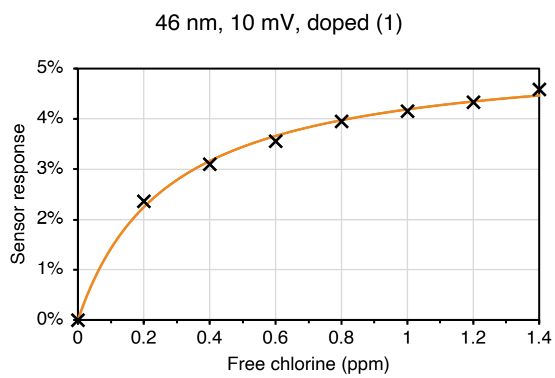


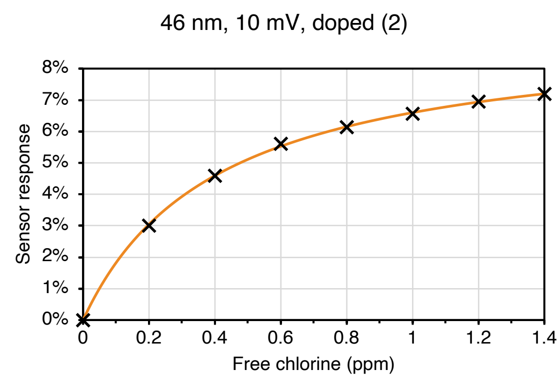

38 nm, 10 mV, doped (1)
Sensor response
0% 1% 2% 3% 4% 5% 6% 7% 8%
0 0.2 0.4 0.6 0.8 1 1.2 1.4
Free chlorine (ppm)

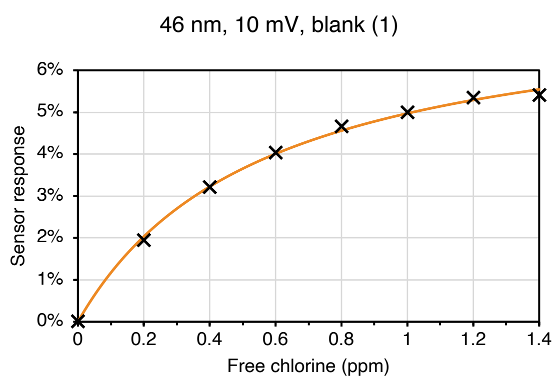

38 nm, 10 mV, doped (2)
Sensor response
0% 1% 2% 3% 4% 5% 6% 7%
0 0.2 0.4 0.6 0.8 1 1.2 1.4
Free chlorine (ppm)

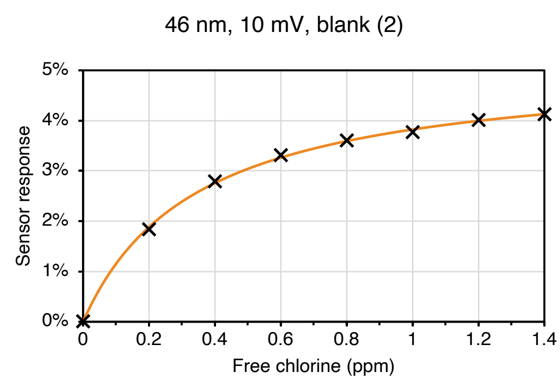

38 nm, 10 mV, blank (1)
Sensor response
0% 1% 2% 3% 4% 5% 6% 7% 8% 9%
0 0.2 0.4 0.6 0.8 1 1.2 1.4
Free chlorine (ppm)


38 nm, 10 mV, blank (2)
Sensor response
0% 1% 2% 3% 4% 5% 6%
0 0.2 0.4 0.6 0.8 1 1.2 1.4
Free chlorine (ppm)

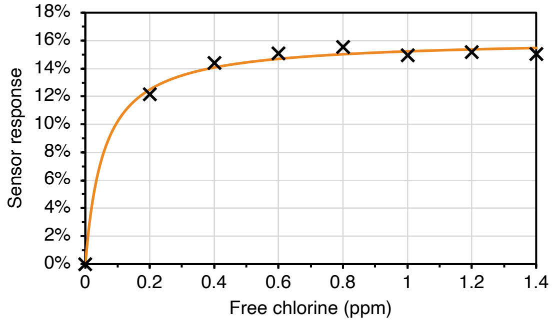

46 nm, 10 mV, doped (1)
Sensor response
0% 1% 2% 3% 4% 5%
0 0.2 0.4 0.6 0.8 1 1.2 1.4
Free chlorine (ppm)


46 nm, 10 mV, doped (2)
Sensor response
0% 1% 2% 3% 4% 5% 6% 7% 8%
0 0.2 0.4 0.6 0.8 1 1.2 1.4
Free chlorine (ppm)

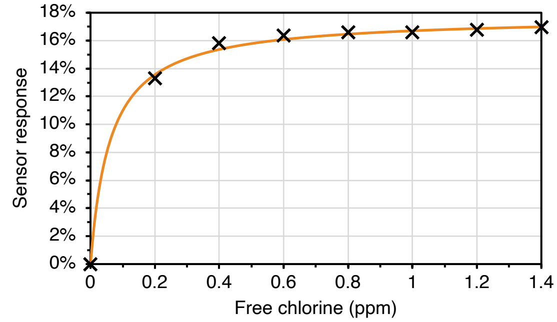

46 nm, 10 mV, blank (1)
Sensor response
0% 1% 2% 3% 4% 5% 6%
0 0.2 0.4 0.6 0.8 1 1.2 1.4
Free chlorine (ppm)


46 nm, 10 mV, blank (2)
Sensor response
0% 1% 2% 3% 4% 5%
0 0.2 0.4 0.6 0.8 1 1.2 1.4
Free chlorine (ppm)

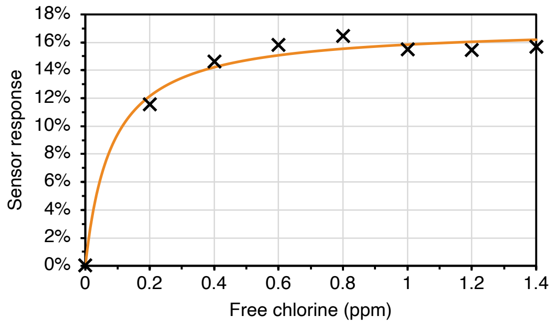
12 nm, 100 mV, doped (1)



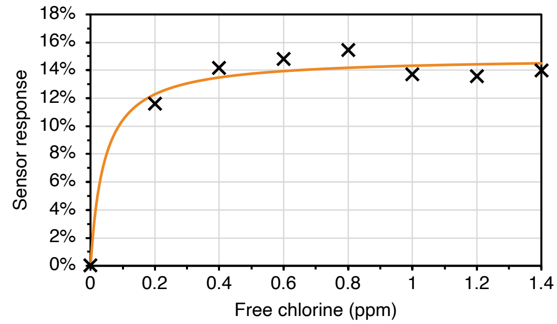
12 nm, 100 mV, doped (2)



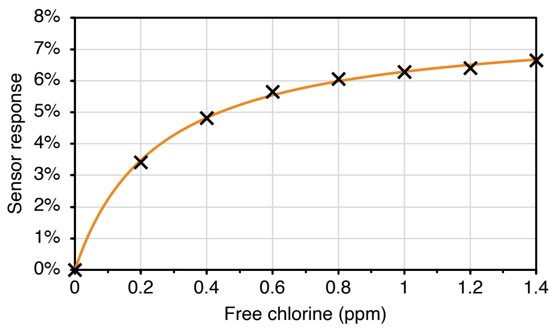
12 nm, 100 mV, blank (1)



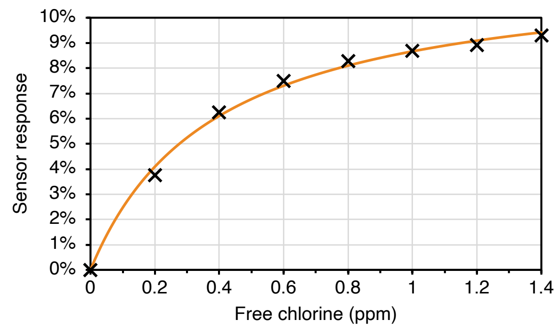
12 nm, 100 mV, blank (2)



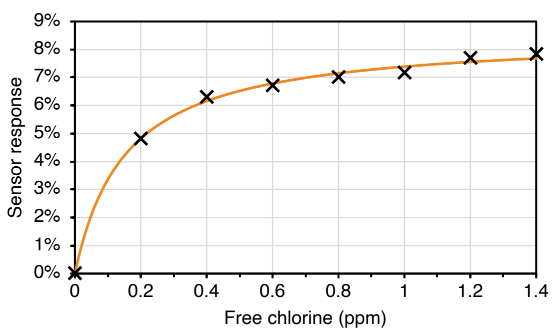
38 nm, 100 mV, doped (1)



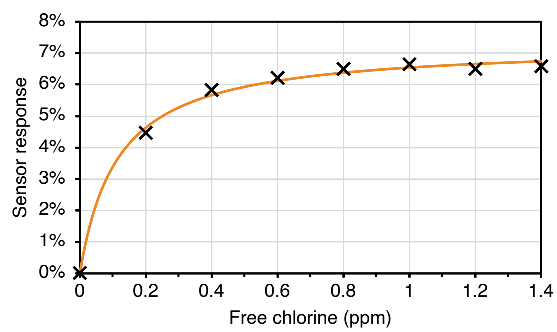
38 nm, 100 mV, doped (2)



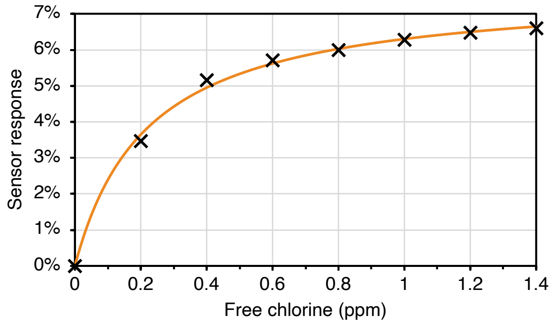
38 nm, 100 mV, blank (1)



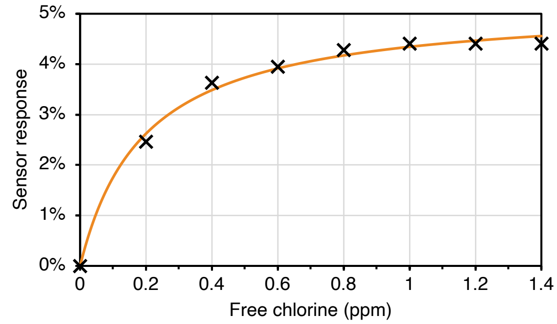
38 nm, 100 mV, blank (2)



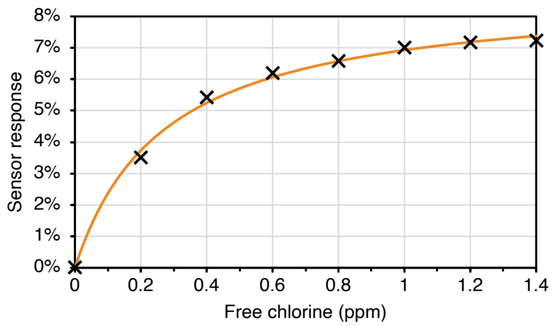
46 nm, 100 mV, doped (1)



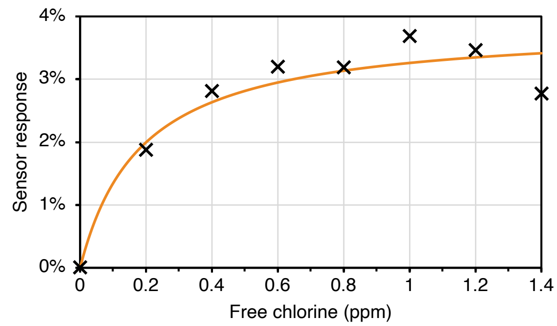
46 nm, 100 mV, doped (2)



46 nm, 100 mV, blank (1)



46 nm, 100 mV, blank (2)



Equation S1. Derivation showing that 1/B is proportional to the saturation concentration (SC). When exposed to the saturation concentration, the sensor response (y) should be equal to the maximum response (A). However, if the sensors are exposed to 95% of the saturation concentration, the sensor response should be 95% of the maximum response. If we rearrange the equation, we get an expression that shows that the saturation concentration is proportional to 1/B.

$$y = \frac{ABx}{1+Bx} \longrightarrow x = \frac{y/A}{1-y/A} \cdot \frac{1}{B} \longrightarrow SC_{95\%} = \frac{0.95}{1-0.95} \cdot \frac{1}{B} \longrightarrow \mathrm{SC} \propto \frac{1}{B}$$

Figure S4. Replicates of the low range detection data (calibration curves and raw data from the lowest concentration).

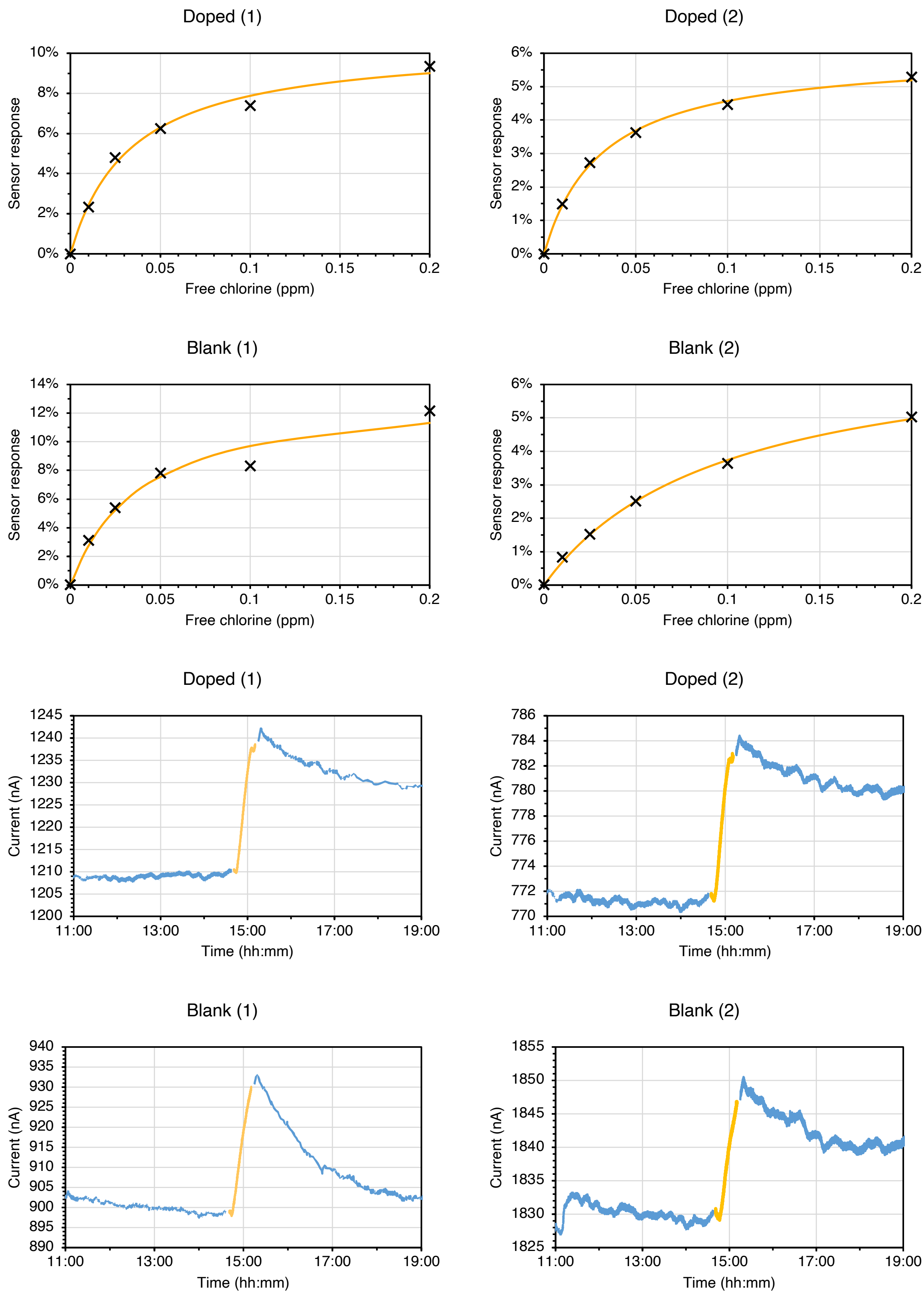
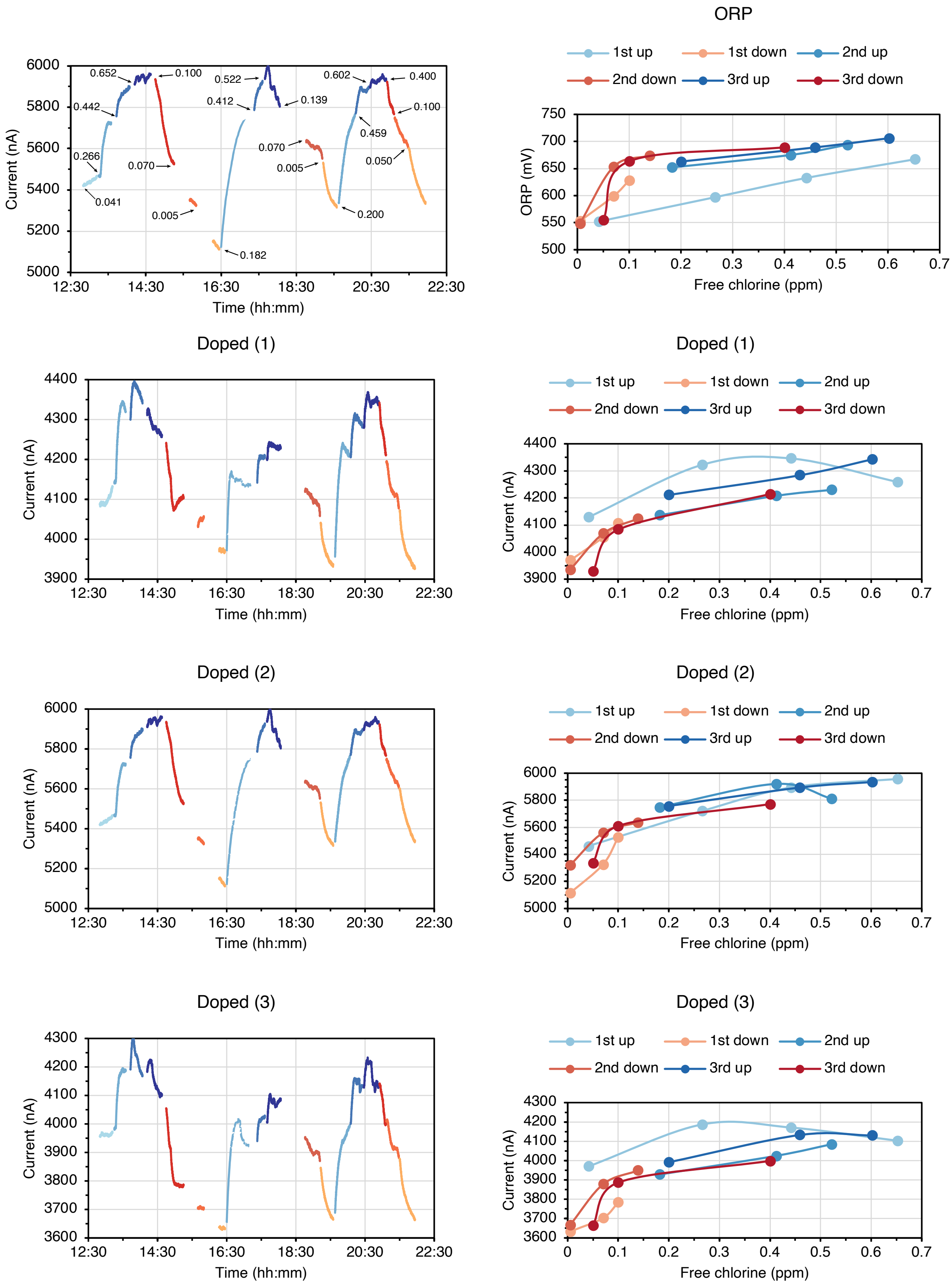
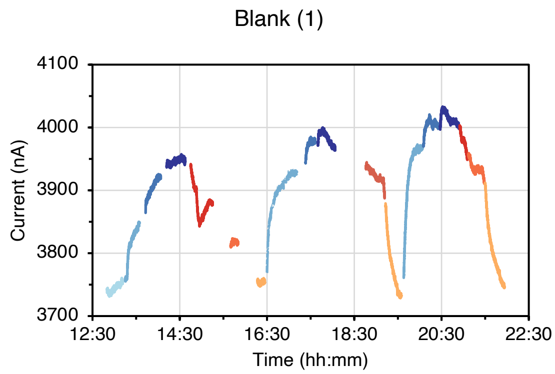


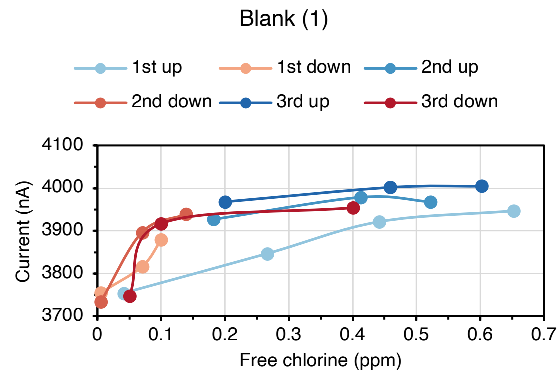
Table S2. Curve parameters from the Langmuir adsorption isotherms used to fit the low range detection data shown in **Figure S4**.

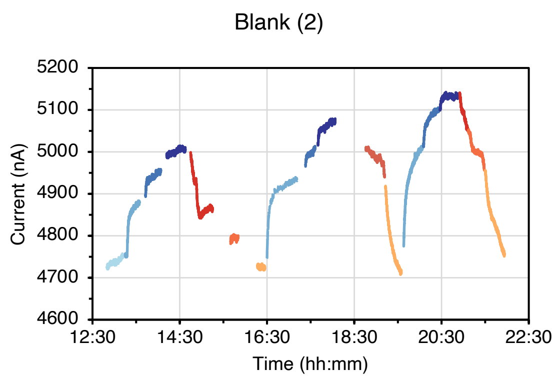
	A	B	R^2
Doped (1)	0.1052	29.8152	0.9922
Doped (2)	0.0601	31.8057	0.9985
Blank (1)	0.1358	25.0066	0.9687
Blank (2)	0.0738	10.2781	0.9978

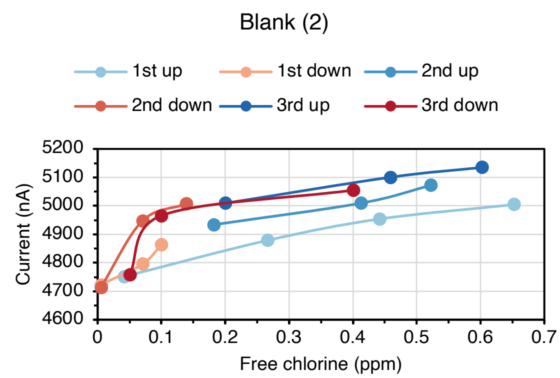
Figure S5. Replicates of the detection of free chlorine concentration fluctuations (raw and processed data). The first graph (top left) uses arrows to display where a new free chlorine concentration was introduced and what the concentration was (measured with the DPD method, AquaMate). The second graph (top right) shows the ORP values for each of those concentrations.

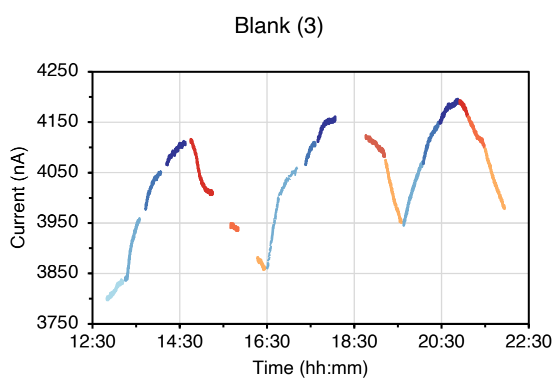



Blank (1)
Current (nA)
4100
4000
3900
3800
3700
12:30
14:30
16:30
18:30
20:30
22:30
Time (hh:mm)


Blank (1)
1st up
1st down
2nd up
2nd down
3rd up
3rd down
Current (nA)
4100
4000
3900
3800
3700
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
Free chlorine (ppm)


Blank (2)
Current (nA)
5200
5100
5000
4900
4800
4700
4600
12:30
14:30
16:30
18:30
20:30
22:30
Time (hh:mm)


Blank (2)
1st up
1st down
2nd up
2nd down
3rd up
3rd down
Current (nA)
5200
5100
5000
4900
4800
4700
4600
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
Free chlorine (ppm)


Blank (3)
Current (nA)
4250
4150
4050
3950
3850
3750
12:30
14:30
16:30
18:30
20:30
22:30
Time (hh:mm)

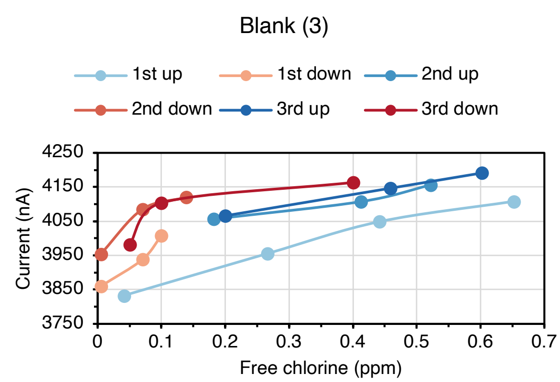

Blank (3)
1st up
1st down
2nd up
2nd down
3rd up
3rd down
Current (nA)
4250
4150
4050
3950
3850
3750
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
Free chlorine (ppm)

Figure S6. Replicate data from the real drinking water testing. The purple cross shows the sensor response to the real water, while the black crosses represent the sensor response to the spiked concentrations.