SUPPLEMENTAL MATERIAL

Chemiresistive detection of silver ions in aqueous media

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Figure S1. Nitrogen 1s high resolution XPS spectra of bathocuproine (left), and the silver-bathocuproine complex (right).

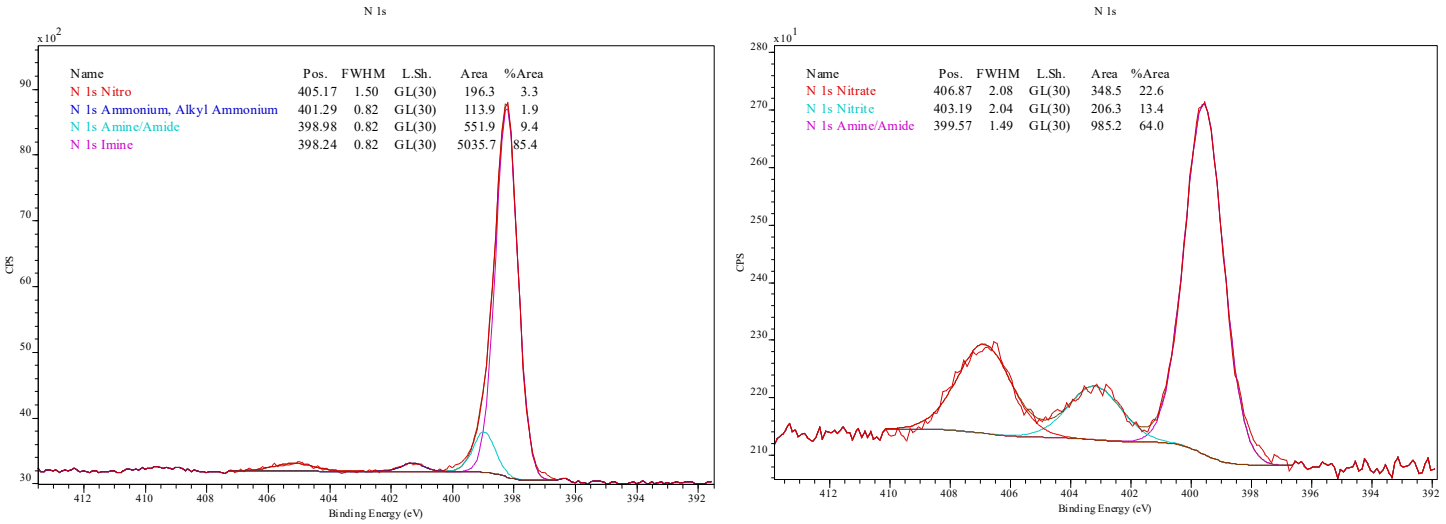


Figure S2. Nitrogen 1s high resolution XPS spectra of the functionalized sensor by itself (left), and the functionalized sensor exposed to silver (right).

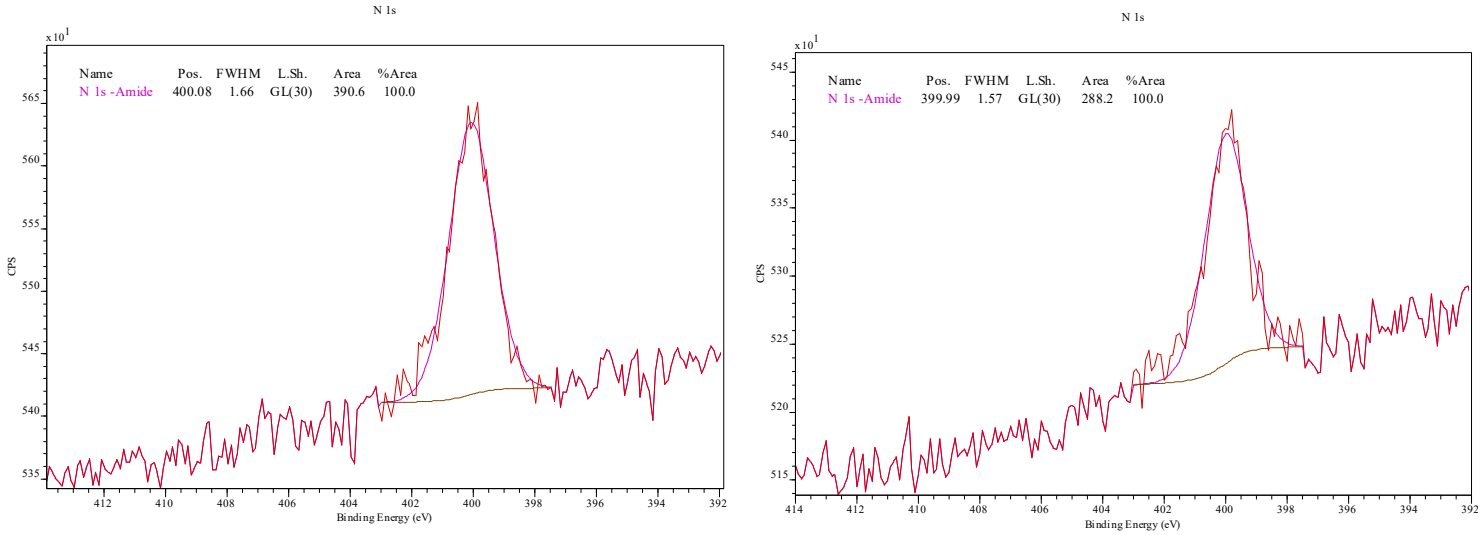


Figure S3. Silver 3d high resolution XPS spectra and Ag MVV Auger peak of the non-functionalized sensor exposed to silver (left), and the functionalized sensor exposed to silver (right).

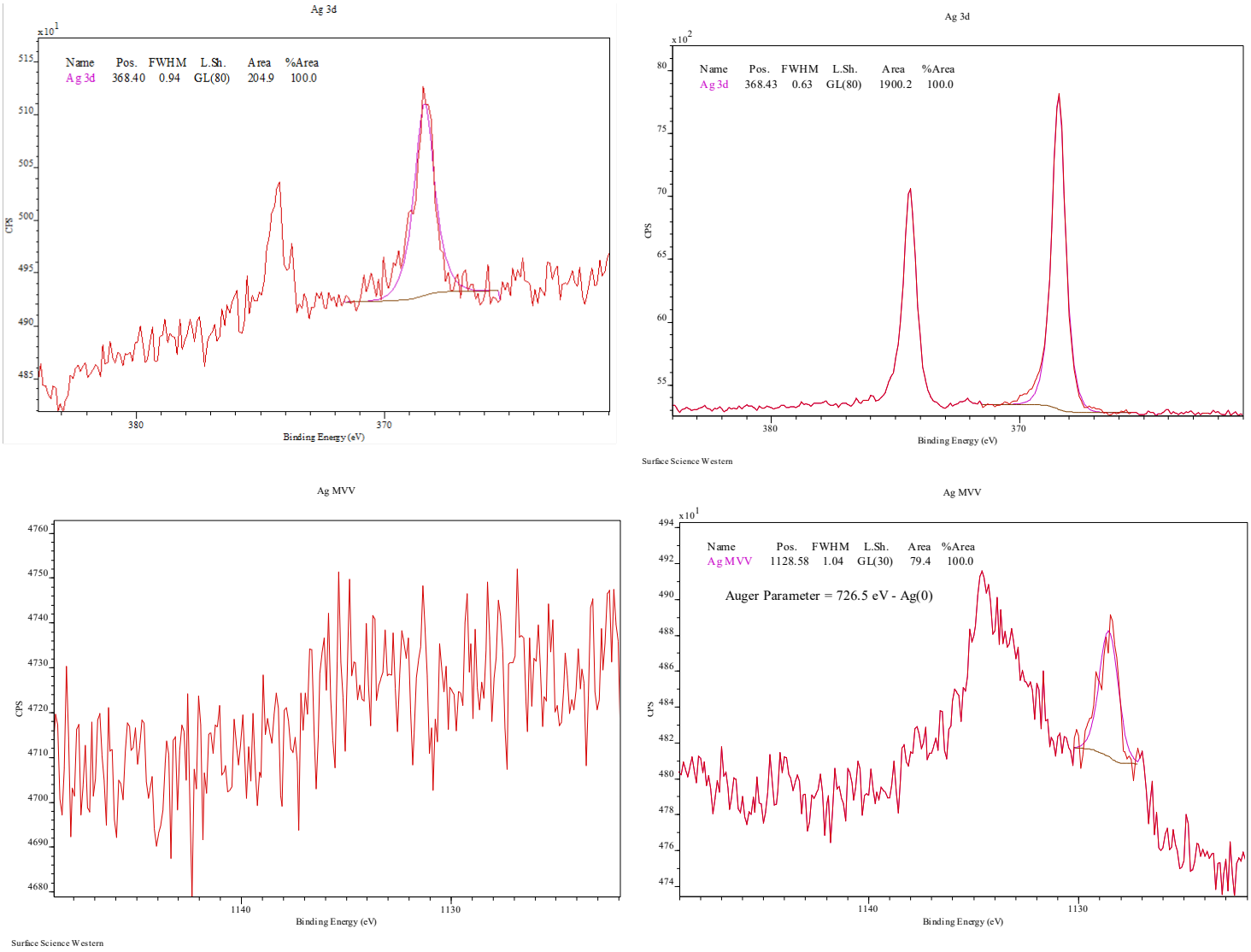


Figure S4. Sensor responses for four bathocuproine functionalized sensors (BC1, BC2, BC3, and BC4), as well as two non-functionalized (blank) sensors. X axes are labelled in the format hour:minutes:seconds. Y axes units are nA (absolute current through the sensor film).

Figure S5. Pictures of the functionalized (left) and the non-functionalized (right) sensor after exposure to 1 ppm silver (I) nitrate in aqueous solution. Metallic silver particles on the non-functionalized sensor film give it a glittery appearance.

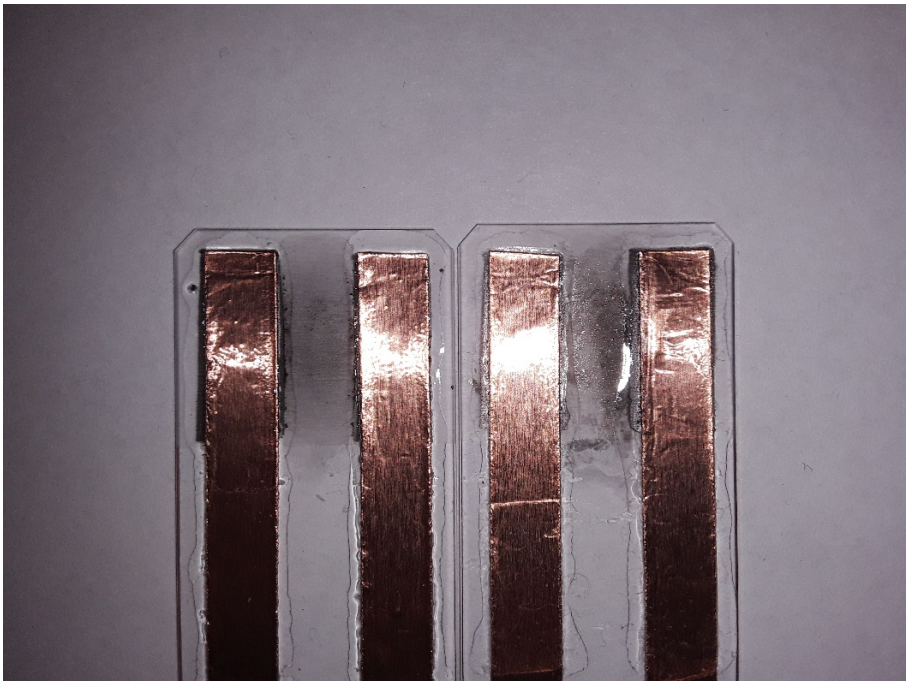


Figure S6. Deposition optimization process of the bathocuproine onto the sensor. The percentage represents the saturation of the bathocuproine in either methanol (MeOH) or acetonitrile (MeCN) solution. X axes are labelled in the format hour:minutes:seconds. Y axes units are nA (absolute current through the sensor film).

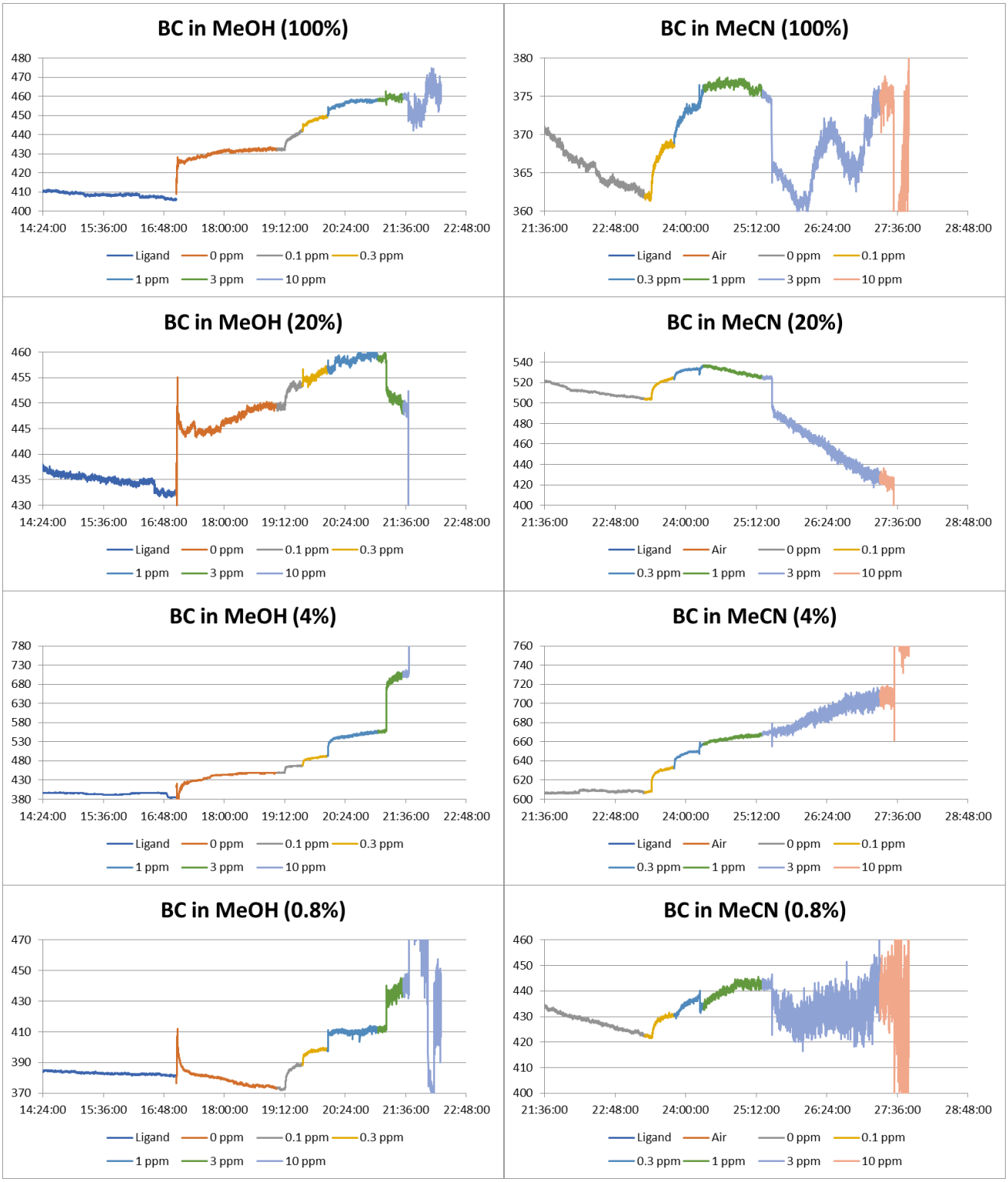
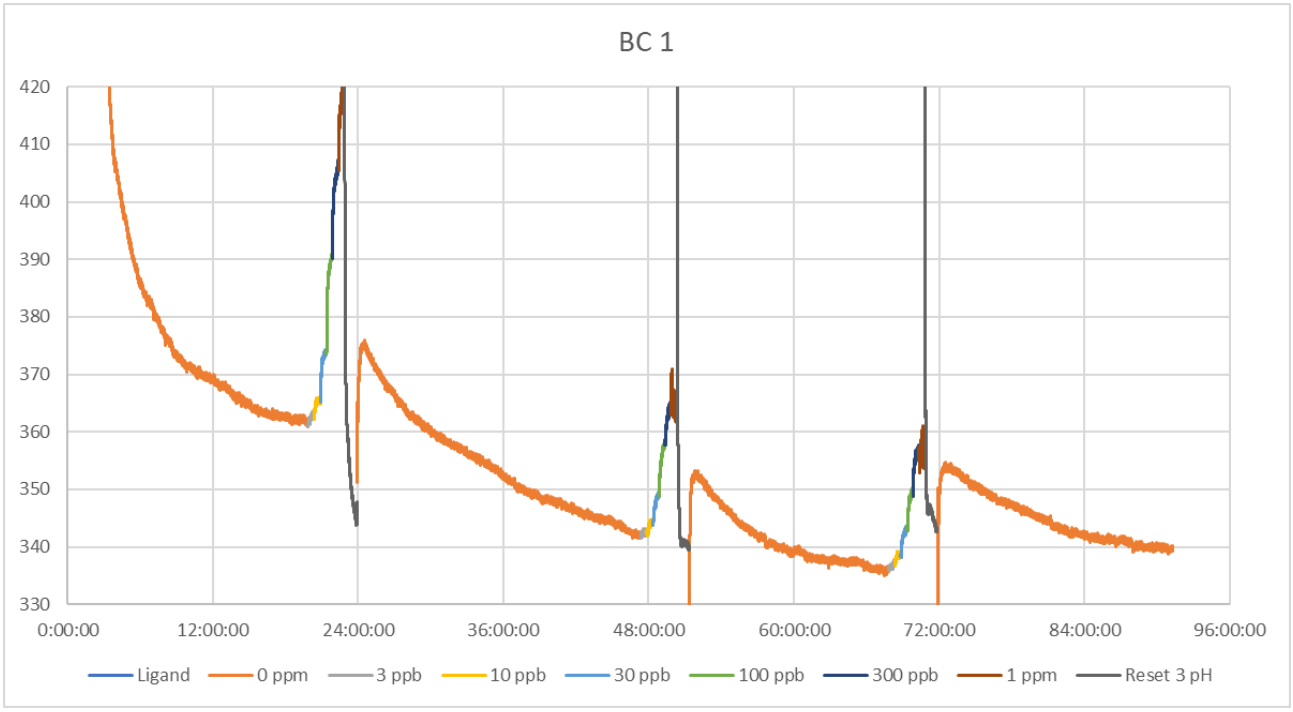
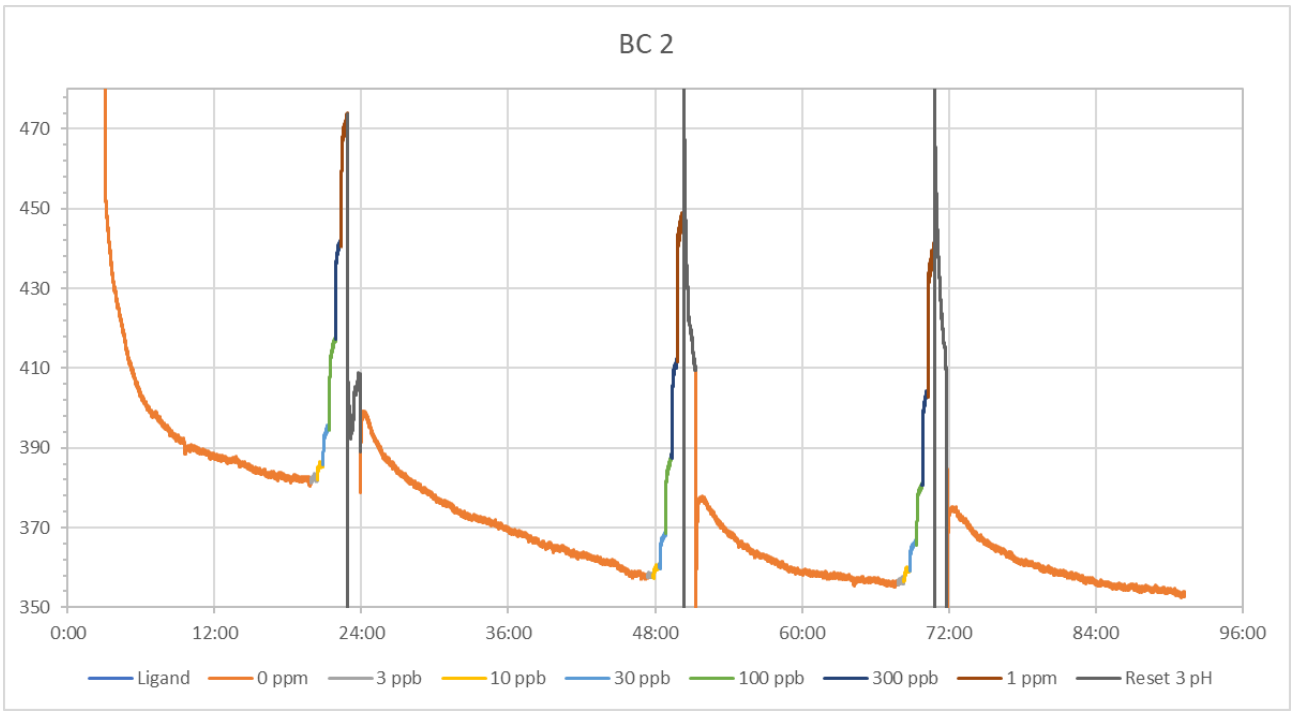
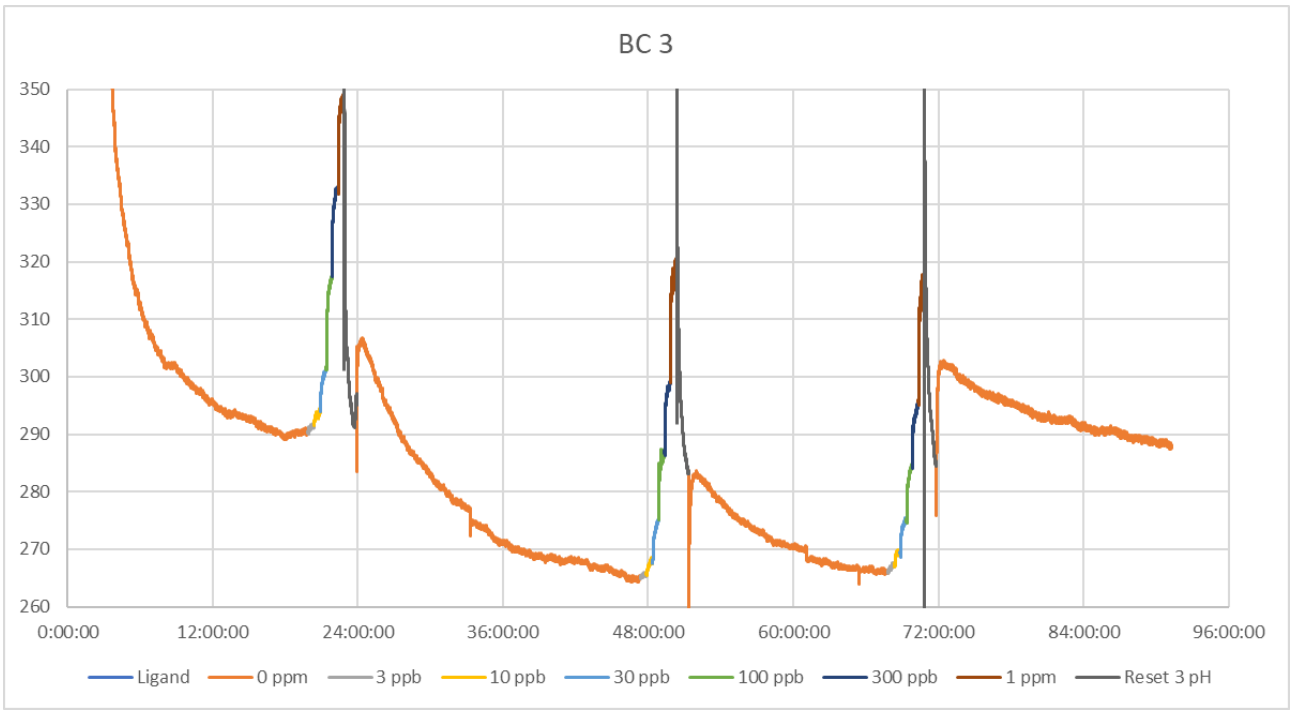


Figure S7. Resetting the four functionalized sensors (BC1, BC2, BC3, and BC4) with pH 3 HNO_3. X axes are labelled in the format hour:minutes:seconds. Y axes units are nA (absolute current through the sensor film).






BC 3
350
340
330
320
310
300
290
280
270
260
0:00:00
12:00:00
24:00:00
36:00:00
48:00:00
60:00:00
72:00:00
84:00:00
96:00:00
Ligand
0 ppm
3 ppb
10 ppb
30 ppb
100 ppb
300 ppb
1 ppm
Reset 3 pH

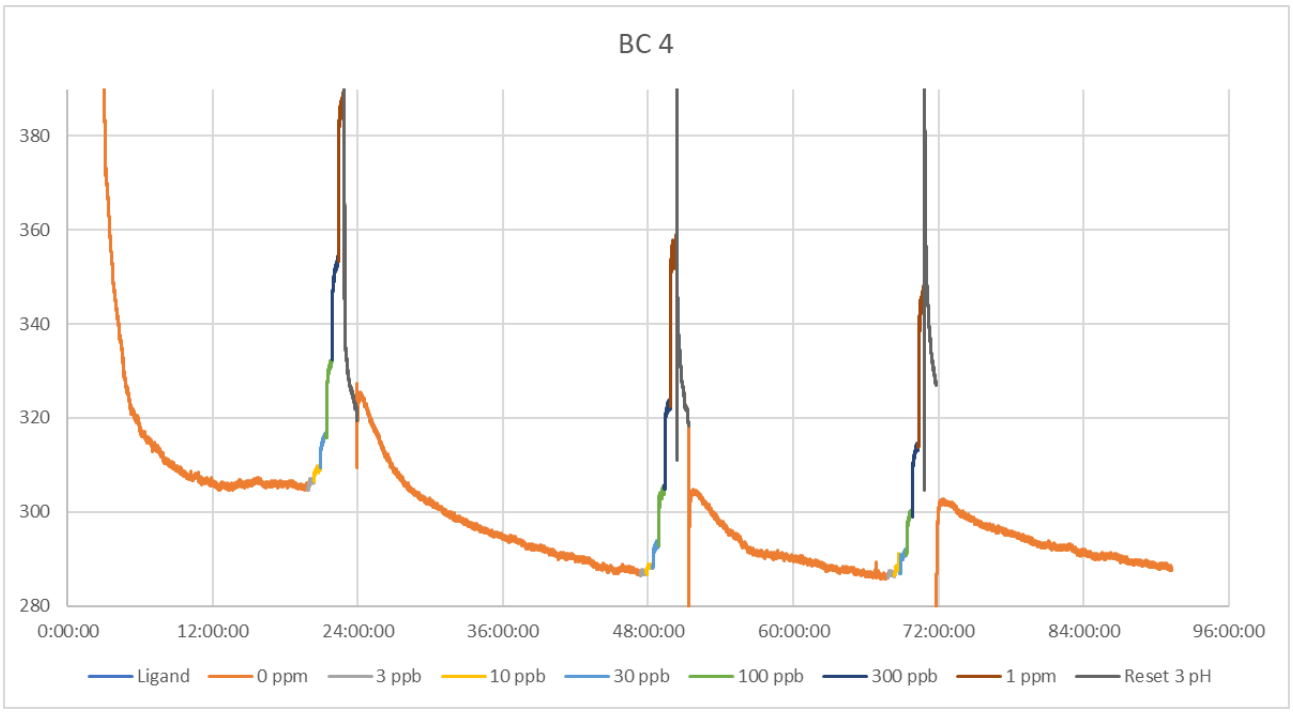

BC 4
380
360
340
320
300
280
0:00:00
12:00:00
24:00:00
36:00:00
48:00:00
60:00:00
72:00:00
84:00:00
96:00:00
Ligand
0 ppm
3 ppb
10 ppb
30 ppb
100 ppb
300 ppb
1 ppm
Reset 3 pH

Figure S8. The linearized response of the Ag^+ sensor. Note that this plot is not appropriate for calibration, its use is to determine the linear range of the sensor.

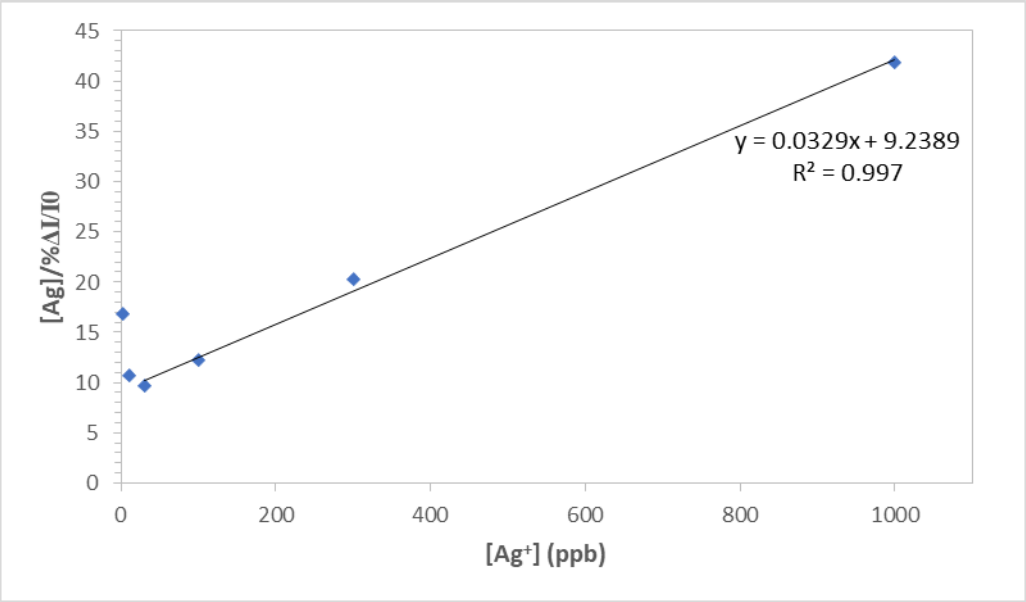


Figure S9. Three replicates of a neocuproine sensor and its response to both copper (II) and silver (I).

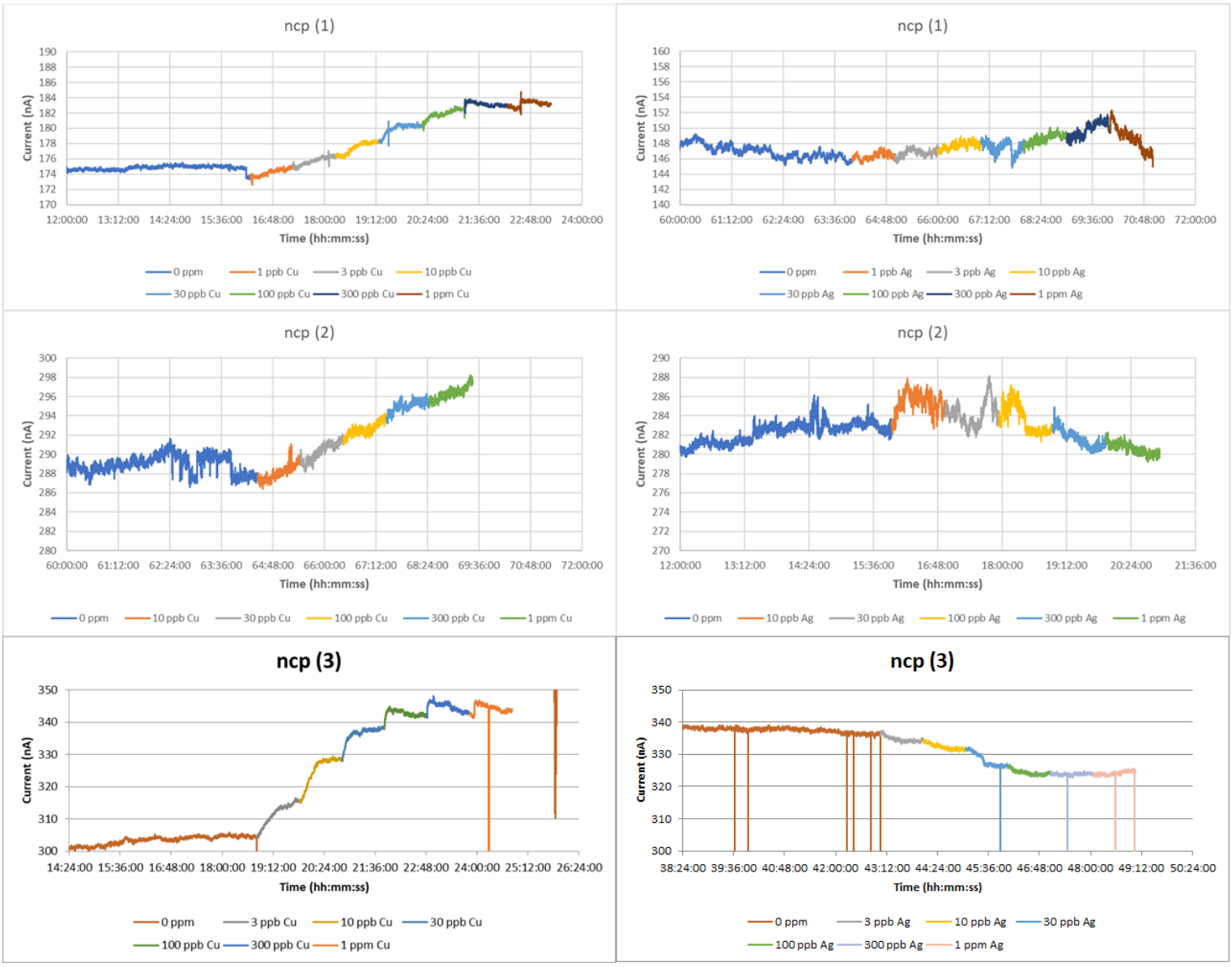
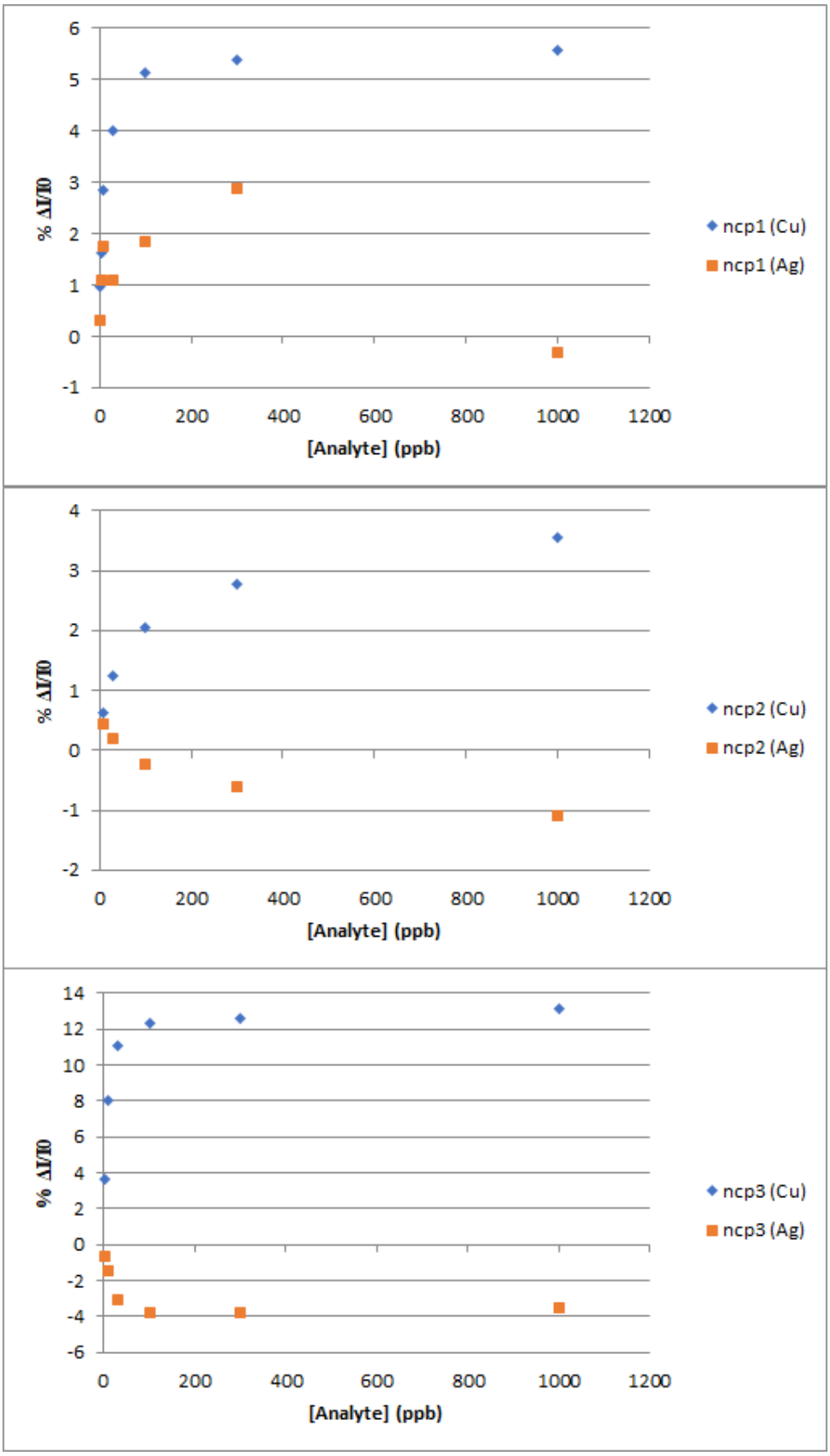


Figure S10. The relative responses of the neocuproine functionalized sensors to both copper (II) and silver (I).



Quality Analysis ... *Innovative Technologies*

Report No.: **A20-08133**
Report Date: **19-Aug-20**
Date Submitted: **23-Jul-20**
Your Reference:

McMaster University
1280 Main Street W
Hamilton Ontario L8S 4M1
Canada

ATTN: Dr Peter Kruse

CERTIFICATE OF ANALYSIS

9 Water samples were submitted for analysis.

The following analytical package(s) were requested:		Testing Date:
6 Total Recoverable (1-50)	QOP HYDROGEO (Total Recoverable Natural Waters with low TDS Hydrogeochemistry ICPMS)	2020-08-19 10:58:23
6-Dissolved Natural (1-50)	QOP HYDROGEO (Natural Waters with low TDS - Hydrogeochemistry ICPMS)	2020-07-30 10:14:21
6B	QOP Anions, EPA 300.1 (Ion Chromatography)	2020-07-24 11:42:13

REPORT **A20-08133**

Notes:

Values which exceed the upper limit should be analysed by Code 6 ICPOES/MS. Samples showing dilution factor had to be diluted for analysis due to high total dissolved solids content. This dilution is taken into account. Detection limits will be elevated on these samples by the dilution factor. Effective October 2013 our Hydro-MS package has been modified with changes to the upper limits of some elements.

CERTIFIED BY:

Emmanuel Eseme , Ph.D.
Quality Control Coordinator

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Analyte Symbol	Na	Li	Be	Mg	Al	Si	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Rb
Unit Symbol	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
Lower Limit	5	1	0.1	2	2	200	30	700	1	0.1	0.1	0.5	0.1	10	0.005	0.3	0.2	0.5	0.01	0.01	0.03	0.2	0.005
Method Code	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
1	58700	10	< 0.1	29300	9	4500	9340	89500	< 1	< 0.1	1.1	< 0.5	1.1	< 10	0.073	2.2	< 0.2	13.7	0.02	0.02	2.10	0.2	3.78
2	57700	9	< 0.1	29300	3	4400	5000	91300	< 1	< 0.1	1.1	< 0.5	0.8	< 10	0.068	1.3	1.6	7.1	0.01	0.02	2.12	0.2	3.63
3	58300	10	< 0.1	29600	4	4500	5110	92200	< 1	< 0.1	1.1	< 0.5	0.9	10	0.067	1.7	1.6	7.4	0.02	0.02	2.15	0.2	3.68
4	60200	9	< 0.1	30800	3	4400	5250	75100	< 1	< 0.1	1.1	< 0.5	0.8	< 10	0.068	1.3	1.6	4.4	0.02	0.02	2.11	0.2	3.72
5	51600	9	< 0.1	26700	7	4200	5410	85600	< 1	< 0.1	1.1	< 0.5	1.0	10	0.083	1.4	1.8	6.6	0.03	0.19	1.82	0.3	3.69
6	61900	10	< 0.1	30900	7	4500	5390	79800	< 1	< 0.1	1.1	< 0.5	1.0	10	0.082	1.5	1.8	4.7	0.03	0.20	1.87	0.3	3.91
7	51200	9	< 0.1	26300	9	4200	4530	84700	< 1	< 0.1	1.0	< 0.5	0.9	10	0.073	1.3	1.7	4.0	0.03	0.20	1.76	0.3	3.61
8	59200	9	< 0.1	29900	7	4200	5170	76500	< 1	< 0.1	1.1	< 0.5	0.4	10	0.075	1.3	1.7	3.4	0.03	0.19	1.78	0.3	3.67
9																							

Analyte Symbol	Sr	Y	Zr	Nb	Mo	Ag	Cd	In	Sn	Sb	Te	Cs	Ba	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho
Unit Symbol	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
Lower Limit	0.04	0.003	0.01	0.005	0.1	0.2	0.01	0.001	0.1	0.01	0.1	0.001	0.1	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Method Code	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
1	918	0.037	0.06	< 0.005	5.7	0.3	0.06	< 0.001	0.4	0.19	< 0.1	0.041	46.3	0.008	0.010	0.008	0.011	0.004	0.002	0.008	< 0.001	0.005	< 0.001
2	920	0.033	0.05	< 0.005	5.7	1.7	< 0.01	< 0.001	0.4	0.18	< 0.1	0.029	47.3	0.004	0.003	0.002	0.010	0.004	0.002	0.006	< 0.001	0.005	< 0.001
3	935	0.034	0.05	< 0.005	5.6	5.7	< 0.01	< 0.001	0.4	0.18	< 0.1	0.022	46.7	0.003	0.004	0.002	0.011	0.004	0.002	0.006	< 0.001	0.005	0.001
4	970	0.036	0.05	< 0.005	5.6	6.9	< 0.01	< 0.001	0.4	0.18	< 0.1	0.022	48.3	0.003	0.004	0.002	0.011	0.004	0.002	0.006	< 0.001	0.005	0.001
5	901	0.072	0.20	0.008	6.0	< 0.2	0.01	0.002	0.6	0.18	< 0.1	0.026	45.8	0.011	0.013	0.011	0.071	0.019	0.024	0.019	0.018	0.071	0.004
6	1050	0.075	0.18	0.009	6.2	23.7	0.01	0.002	0.6	0.18	< 0.1	0.028	54.3	0.012	0.014	0.011	0.075	0.021	0.025	0.020	0.019	0.075	0.004
7	899	0.070	0.17	0.008	5.8	45.2	0.01	0.002	0.5	0.17	< 0.1	0.028	46.6	0.012	0.014	0.011	0.071	0.019	0.024	0.018	0.019	0.072	0.004
8	1030	0.073	0.17	0.008	5.8	81.0	< 0.01	0.002	0.6	0.18	< 0.1	0.019	52.3	0.011	0.012	0.011	0.072	0.019	0.026	0.018	0.019	0.074	0.004
9																							

Analyte Symbol	Er	Tm	Yb	Lu	Hf	Ta	W	Hg	Tl	Pb	Bi	Th	U	F	Cl	NO2 (as N)	Br	NO3 (as N)	PO4 (as P)	SO4
Unit Symbol	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Lower Limit	0.001	0.001	0.001	0.001	0.001	0.001	0.02	0.2	0.001	0.01	0.3	0.001	0.001	0.01	0.03	0.01	0.03	0.01	0.02	0.03
Method Code	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	IC	IC	IC	IC	IC	IC	IC
1	0.003	< 0.001	0.002	< 0.001	< 0.001	< 0.001	< 0.02	< 0.2	0.022	0.21	< 0.3	< 0.001	1.18							
2	0.003	< 0.001	0.002	< 0.001	< 0.001	< 0.001	< 0.02	< 0.2	0.021	< 0.01	< 0.3	< 0.001	1.17							
3	0.003	< 0.001	0.002	< 0.001	< 0.001	< 0.001	< 0.02	< 0.2	0.021	< 0.01	< 0.3	< 0.001	1.18							
4	0.003	< 0.001	0.002	< 0.001	< 0.001	< 0.001	< 0.02	< 0.2	0.021	< 0.01	< 0.3	< 0.001	1.19							
5	0.010	0.013	0.008	0.137	0.001	0.001	0.05	< 0.2	0.023	1.60	< 0.3	0.003	1.36							
6	0.011	0.014	0.008	0.143	0.001	0.001	0.06	< 0.2	0.026	0.10	< 0.3	0.002	1.45							
7	0.010	0.013	0.008	0.137	< 0.001	0.001	0.05	< 0.2	0.024	0.09	< 0.3	0.002	1.34							
8	0.011	0.014	0.008	0.143	< 0.001	0.001	0.05	< 0.2	0.024	0.09	< 0.3	0.002	1.34							
9														0.12	103	< 0.05	0.18	0.79	< 0.1	64.1

Analyte Symbol	Na	Li	Be	Mg	Al	Si	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Rb
Unit Symbol	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
Lower Limit	5	1	0.1	2	2	200	30	700	1	0.1	0.1	0.5	0.1	10	0.005	0.3	0.2	0.5	0.01	0.01	0.03	0.2	0.005
Method Code	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
IC Ref Std Meas																							
IC Ref Std Cert																							
IC Ref Std Meas																							
IC Ref Std Cert																							
IV-STOCK-1643 (ICP/MS) Meas	24100	19	13.4	8970	156		2290	36000			42.2	20.6	41.1	110	30.6	62.2	23.0	64.8			54.7	7.7	15.1
IV-STOCK-1643 (ICP/MS) Cert	21000	17.0	14.0	8000	142		2000	32000			38.0	20.0	39.0	98.0	27.0	62.0	23.0	79.0			60.0	12.0	14.0
IV-STOCK-1643 (ICP/MS) Meas	24100	19	13.4	8970	156		2290	36000			42.2	20.6	41.1	110	30.6	62.2	23.0	64.8			54.7	7.7	15.1
IV-STOCK-1643 (ICP/MS) Cert	21000	17.0	14.0	8000	142		2000	32000			38.0	20.0	39.0	98.0	27.0	62.0	23.0	79.0			60.0	12.0	14.0
9 Orig																							
9 Dup																							
Method Blank																							
Method Blank																							
Method Blank	< 5	< 1	< 0.1	< 2	< 2	< 200	< 30	< 700	< 1	< 0.1	< 0.1	< 0.5	< 0.1	< 10	< 0.005	< 0.3	< 0.2	< 0.5	< 0.01	< 0.01	< 0.03	< 0.2	< 0.005
Method Blank	< 5	< 1	< 0.1	< 2	< 2	< 200	< 30	< 700	< 1	< 0.1	< 0.1	< 0.5	< 0.1	< 10	< 0.005	< 0.3	< 0.2	< 0.5	< 0.01	< 0.01	< 0.03	< 0.2	< 0.005

Analyte Symbol	Sr	Y	Zr	Nb	Mo	Ag	Cd	In	Sn	Sb	Te	Cs	Ba	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho
Unit Symbol	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
Lower Limit	0.04	0.003	0.01	0.005	0.1	0.2	0.01	0.001	0.1	0.01	0.1	0.001	0.1	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Method Code	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
IC Ref Std Meas																							
IC Ref Std Cert																							
IC Ref Std Meas																							
IC Ref Std Cert																							
IV-STOCK-1643 (ICP/MS) Meas	355				137	0.9	6.25			54.3	0.8		576										
IV-STOCK-1643 (ICP/MS) Cert	323				121	1.00	7.00			58.0	1.00		544										
IV-STOCK-1643 (ICP/MS) Meas	355				137	0.9	6.25			54.3	0.8		576										
IV-STOCK-1643 (ICP/MS) Cert	323				121	1.00	7.00			58.0	1.00		544										
9 Orig																							
9 Dup																							
Method Blank																							
Method Blank																							
Method Blank	< 0.04	< 0.003	< 0.01	< 0.005	< 0.1	< 0.2	< 0.01	< 0.001	< 0.1	< 0.01	< 0.1	< 0.001	< 0.1	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Method Blank	< 0.04	< 0.003	< 0.01	< 0.005	< 0.1	< 0.2	< 0.01	< 0.001	< 0.1	< 0.01	< 0.1	< 0.001	< 0.1	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001

Analyte Symbol	Er	Tm	Yb	Lu	Hf	Ta	W	Hg	Tl	Pb	Bi	Th	U	F	Cl	NO2 (as N)	Br	NO3 (as N)	PO4 (as P)	SO4
Unit Symbol	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Lower Limit	0.001	0.001	0.001	0.001	0.001	0.001	0.02	0.2	0.001	0.01	0.3	0.001	0.001	0.01	0.03	0.01	0.03	0.01	0.02	0.03
Method Code	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	IC	IC	IC	IC	IC	IC	IC
IC Ref Std Meas														2.09	14.9	3.04	9.84	2.96	4.75	14.8
IC Ref Std Cert														2.00	15.0	3.01	10.0200	3.01	5.01	15.0
IC Ref Std Meas														2.04	15.0	3.06	9.99	3.02	4.89	14.9
IC Ref Std Cert														2.00	15.0	3.01	10.0200	3.01	5.01	15.0
IV-STOCK-1643 (ICP/MS) Meas									6.88	19.6	13.5									
IV-STOCK-1643 (ICP/MS) Cert									7.00	20.0	14.0									
IV-STOCK-1643 (ICP/MS) Meas									6.88	19.6	13.5									
IV-STOCK-1643 (ICP/MS) Cert									7.00	20.0	14.0									
9 Orig														0.12	104	< 0.05	0.18	0.79	< 0.1	64.1
9 Dup														0.12	103	< 0.05	0.18	0.79	< 0.1	64.0
Method Blank														< 0.01	< 0.03	< 0.01	< 0.03	< 0.01	< 0.02	< 0.03
Method Blank														< 0.01	< 0.03	< 0.01	< 0.03	< 0.01	< 0.02	< 0.03
Method Blank	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.02	< 0.2	< 0.001	< 0.01	< 0.3	< 0.001	< 0.001							
Method Blank	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.02	< 0.2	< 0.001	< 0.01	< 0.3	< 0.001	< 0.001							