Development of geochemical sensors for continuous, on-line monitoring and modelling of coastal groundwater aquifers

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Appendix A and B

to the Ph.D. Dissertation:

Development of geochemical sensors for continuous, on-line monitoring and modelling of coastal groundwater aquifers

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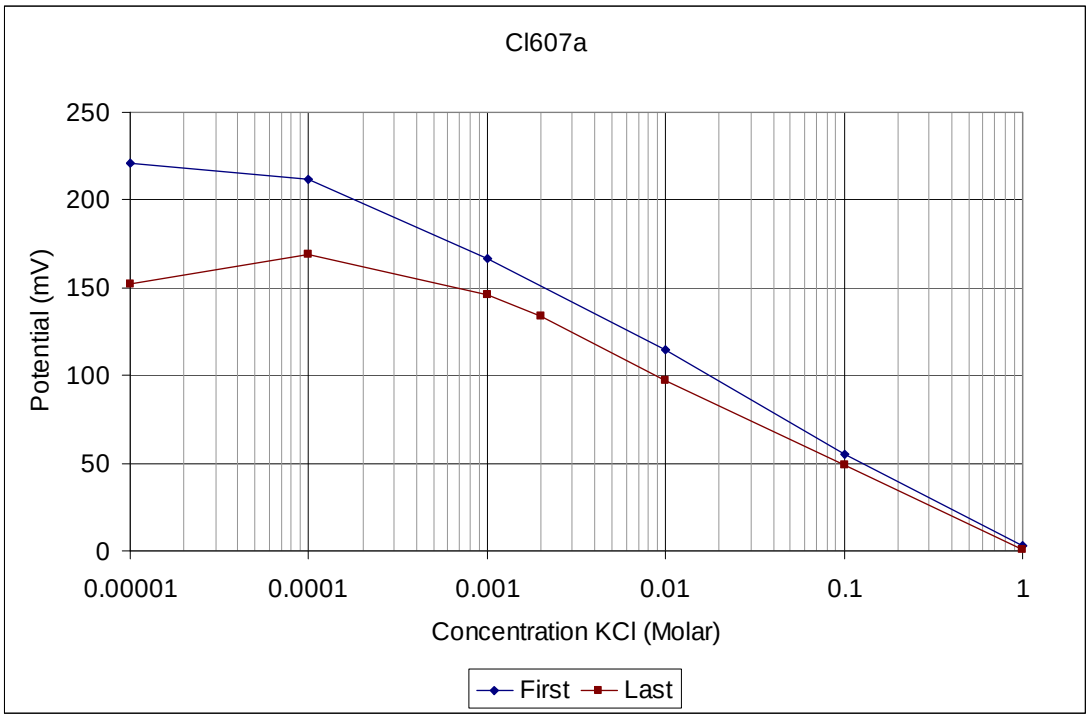
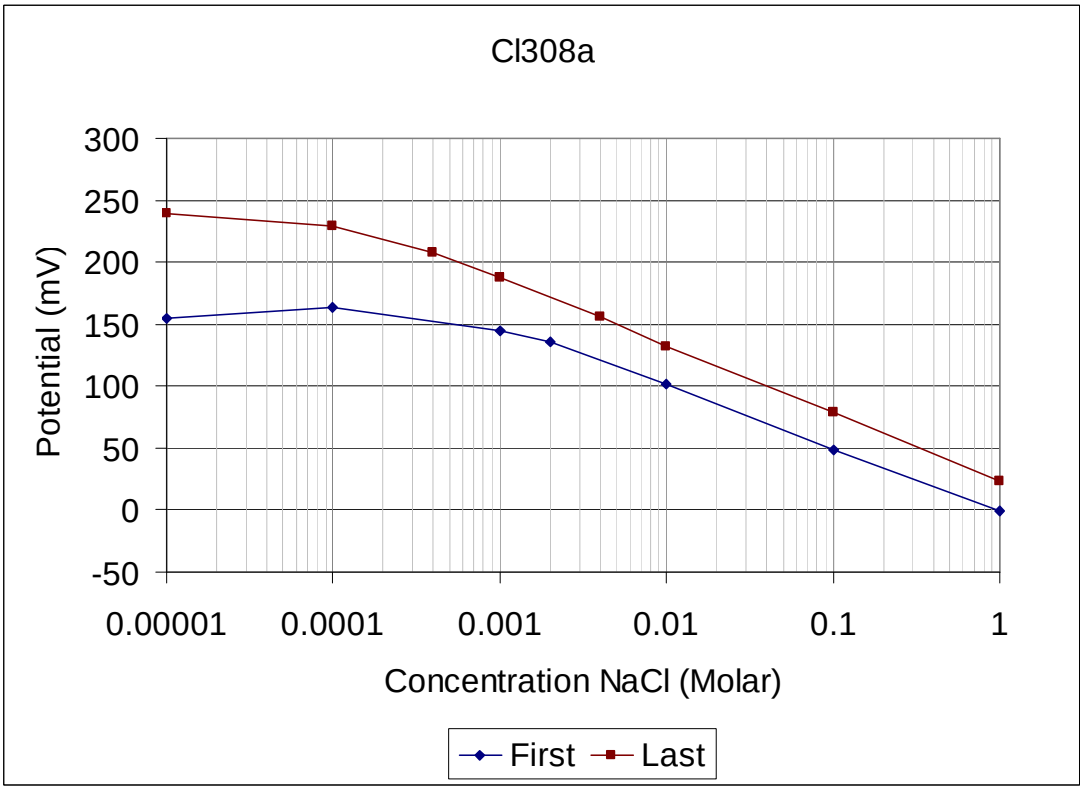
Roskilde University

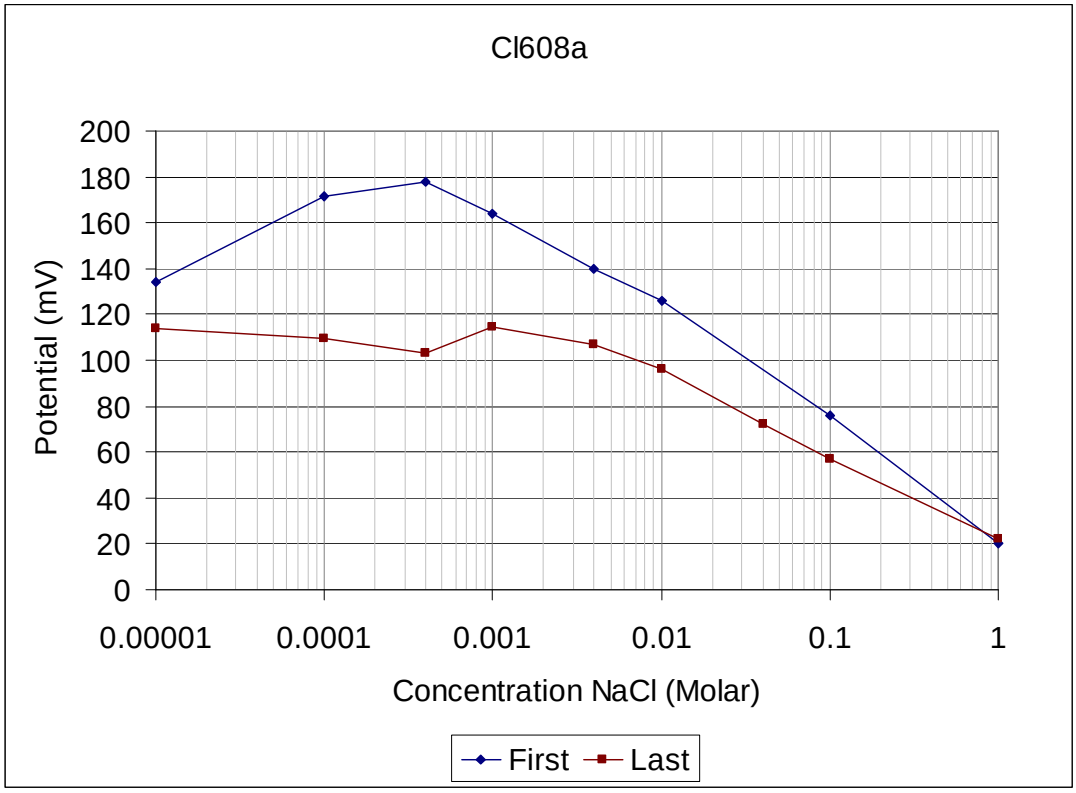
June, 2010

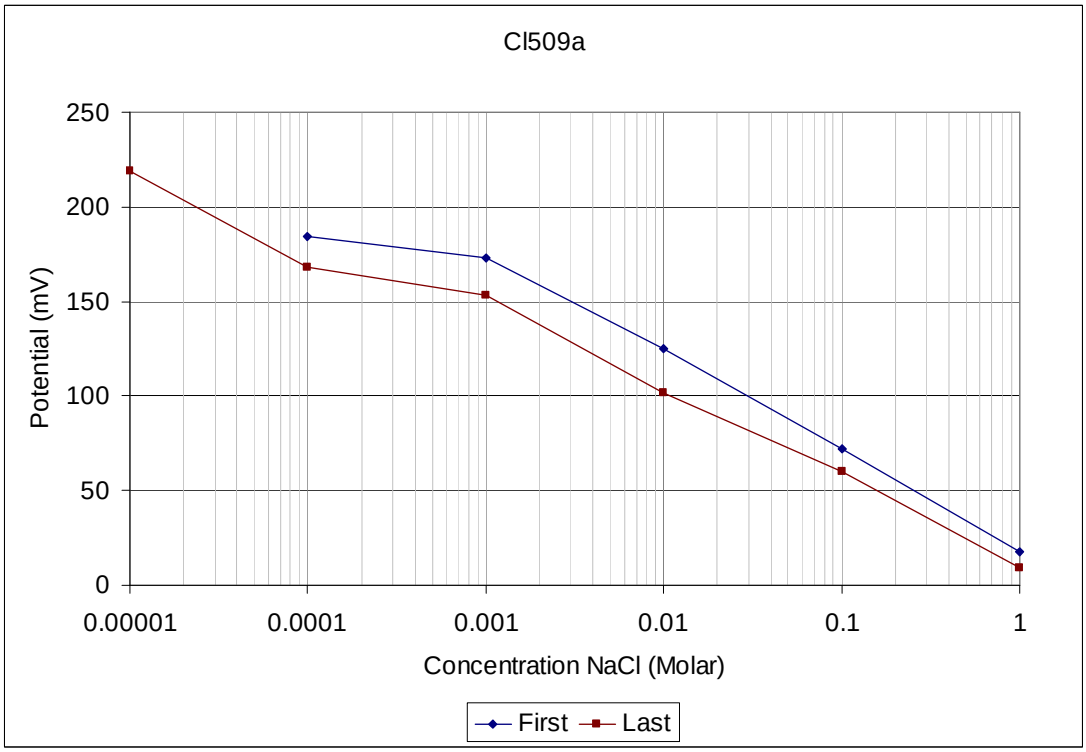
Appendix A
Chloride Sensor Data

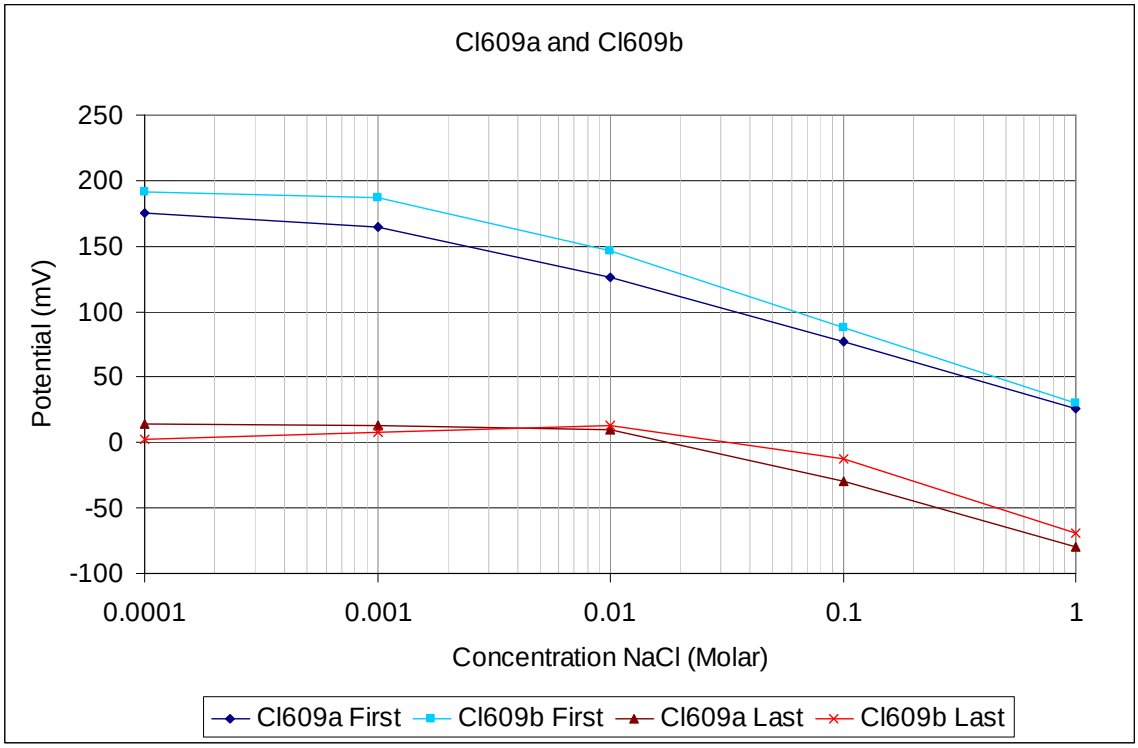
A1. Calibration data, as associated with Table 1 in Chapter 3.



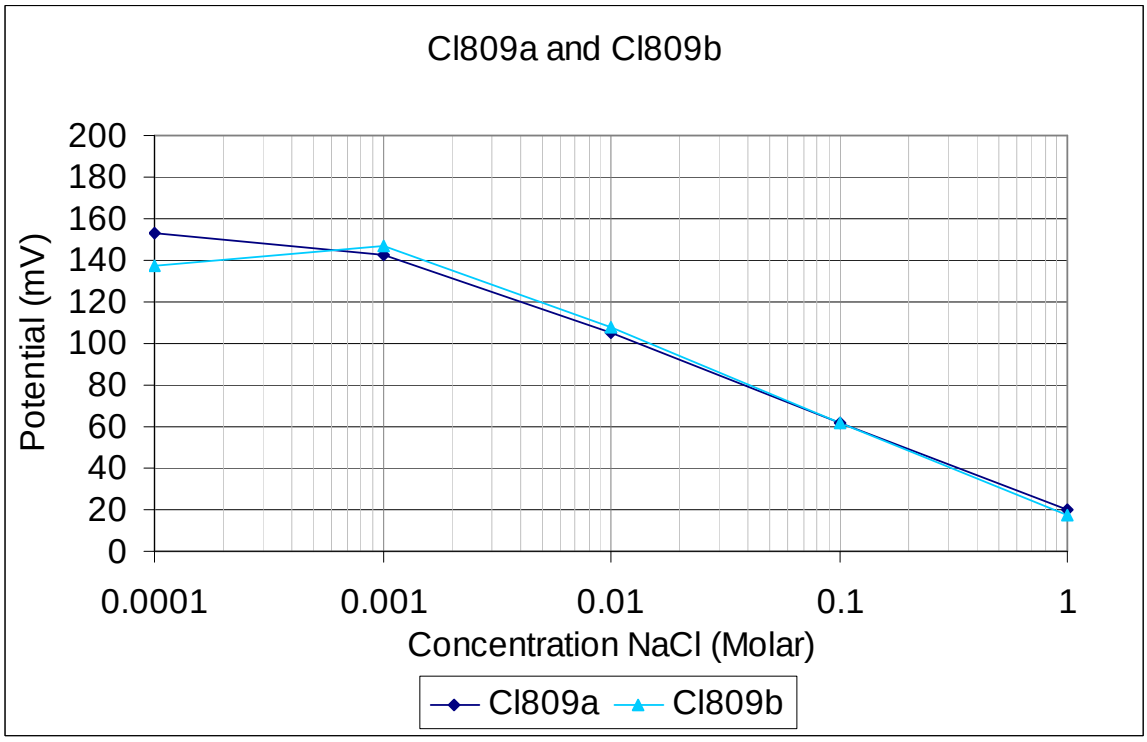



Cl608a
Potential (mV)
200
180
160
140
120
100
80
60
40
20
0
0.00001
0.0001
0.001
0.01
0.1
1
Concentration NaCl (Molar)
First
Last

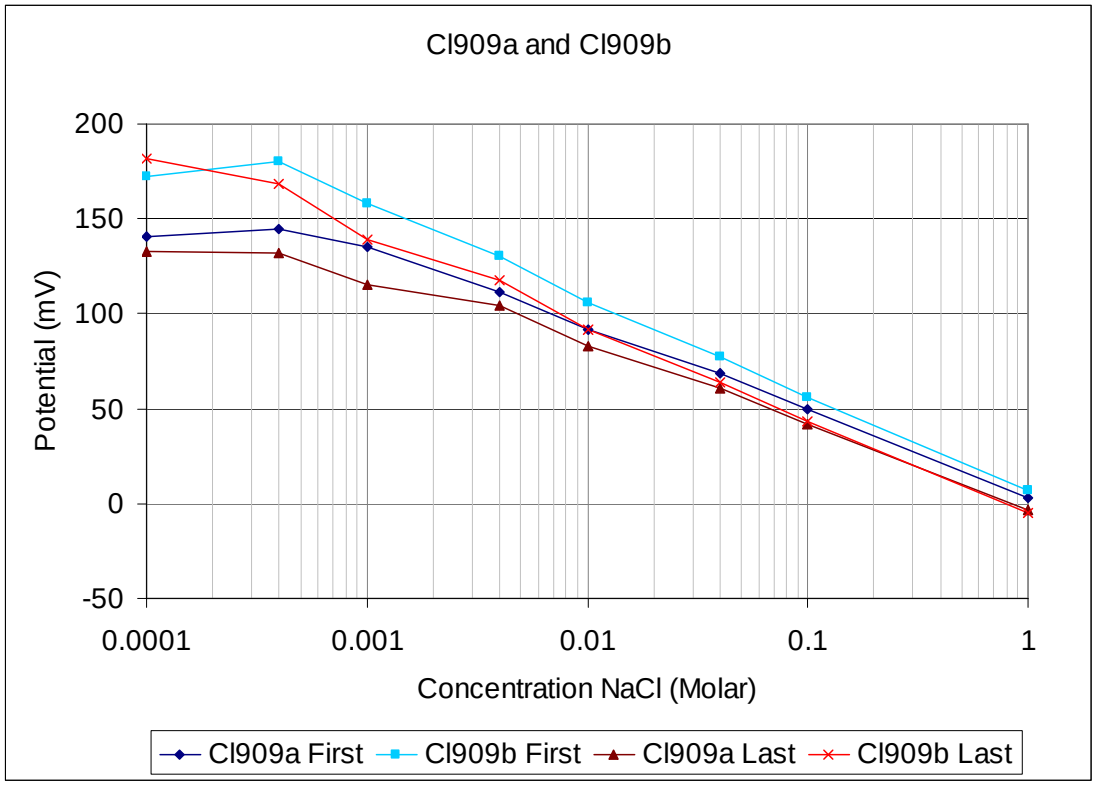

Cl509a
Potential (mV)
250
200
150
100
50
0
0.00001
0.0001
0.001
0.01
0.1
1
Concentration NaCl (Molar)
First
Last



Note: the last measurements conducted on this sensor was after the June/July test in the Greve monitoring well, where the sensors were covered with a bright orange layer of ochre.

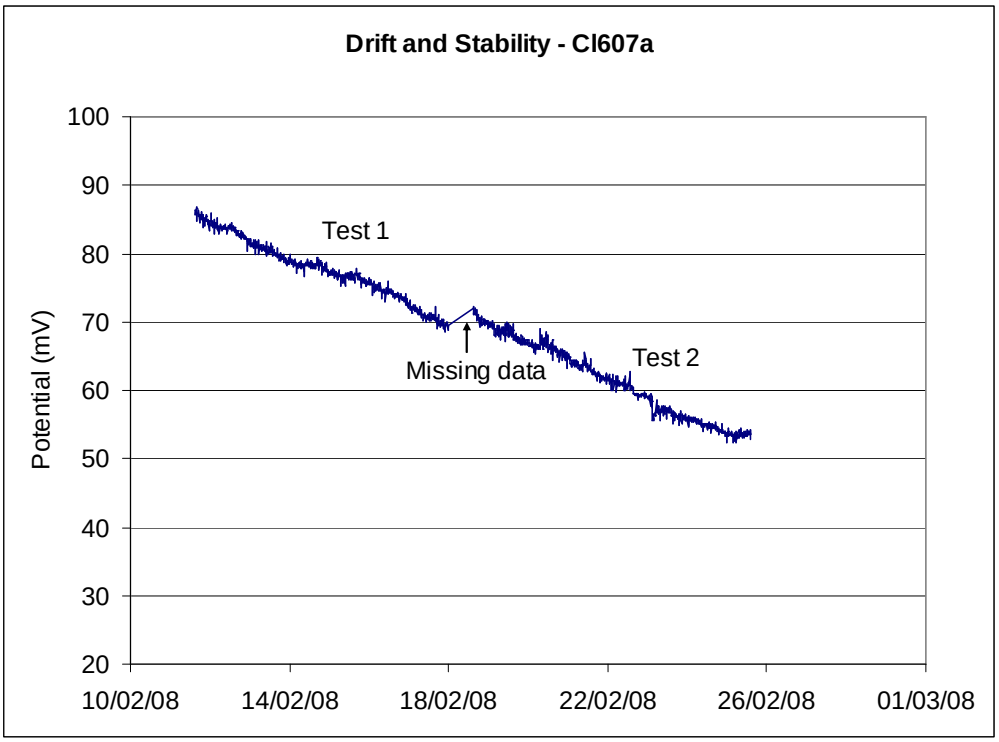


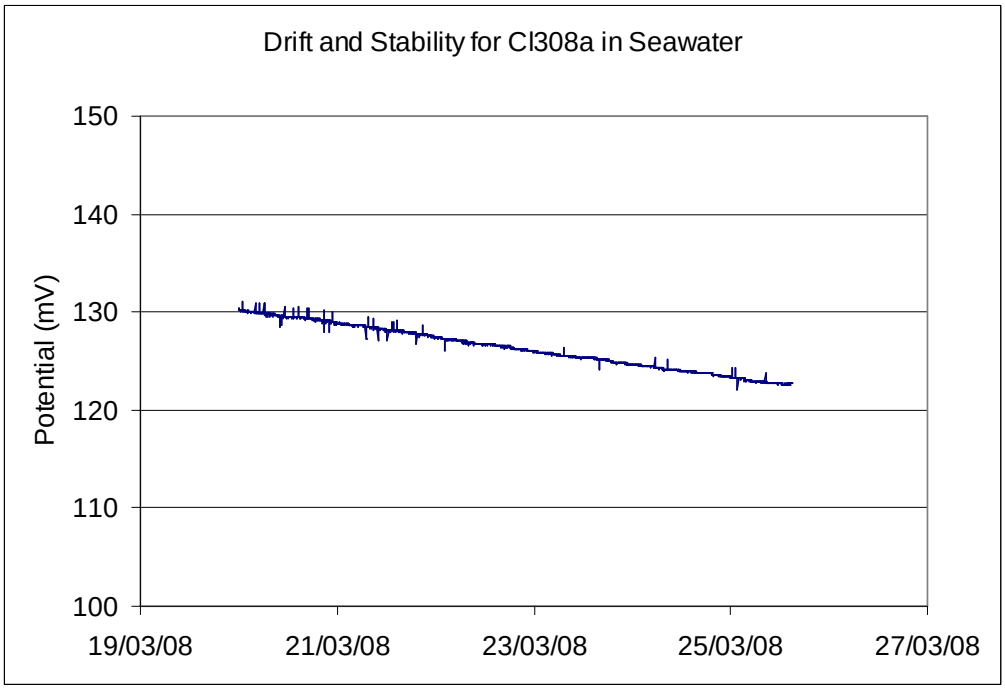
Note: the sensors were used in the August and September Greve monitoring well tests, and no post-test calibration was conducted for these sensors.

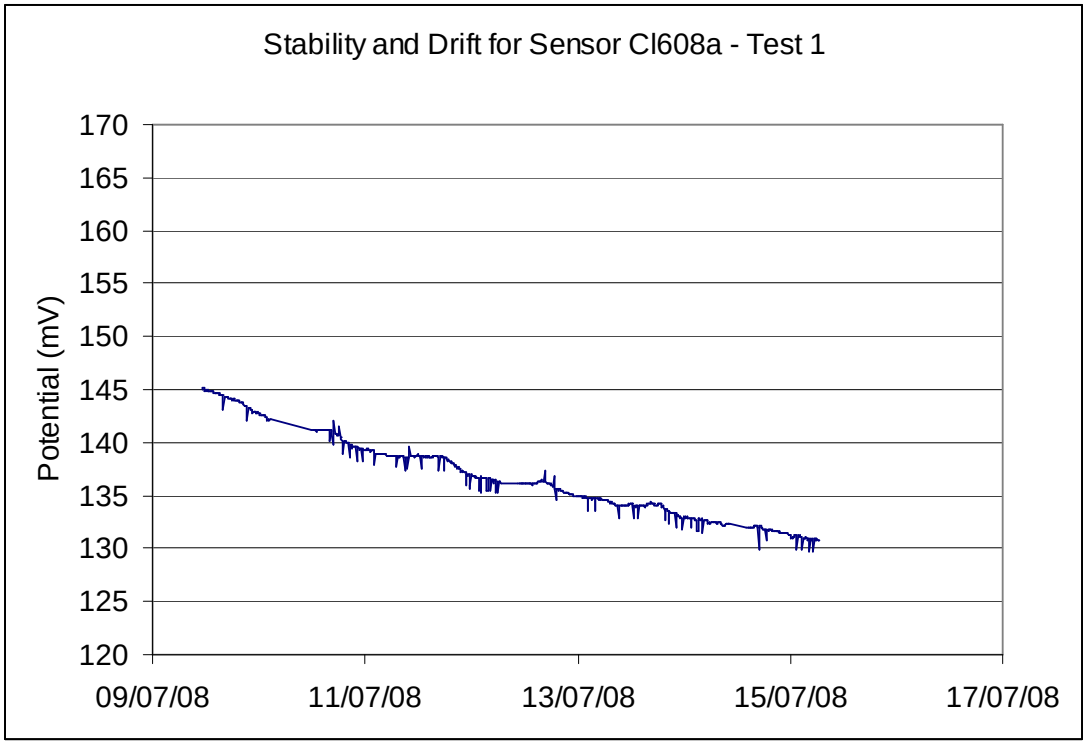


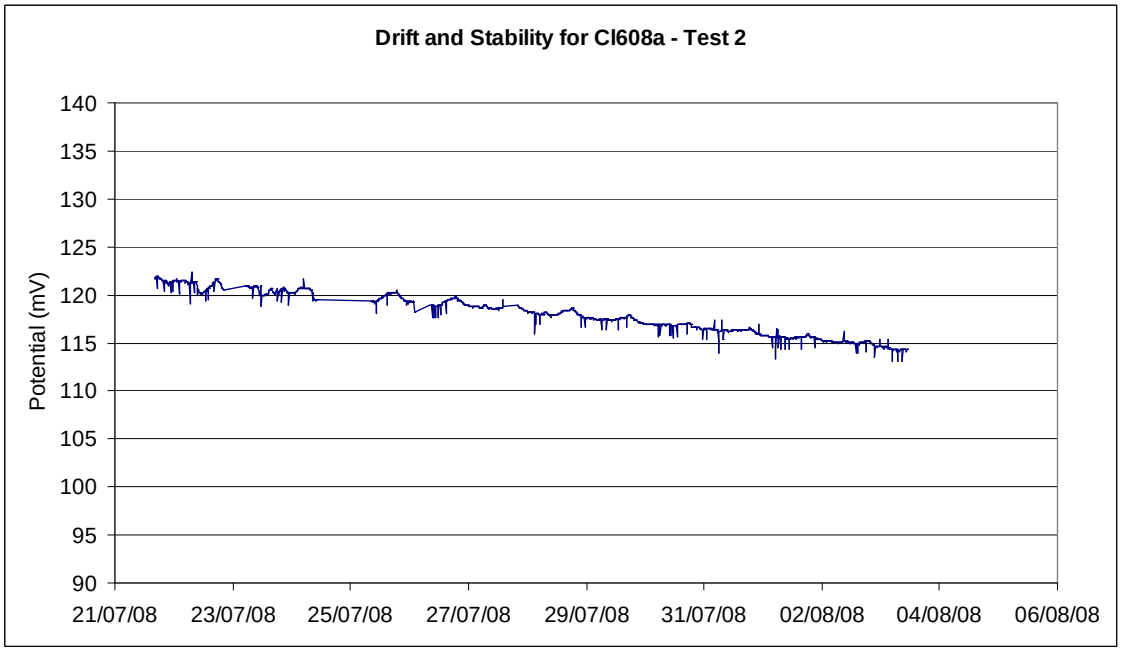
Note: the measurements show the calibration before the sensors were used in the Wickford monitoring test, and then show the last measurement taken for the sensors.

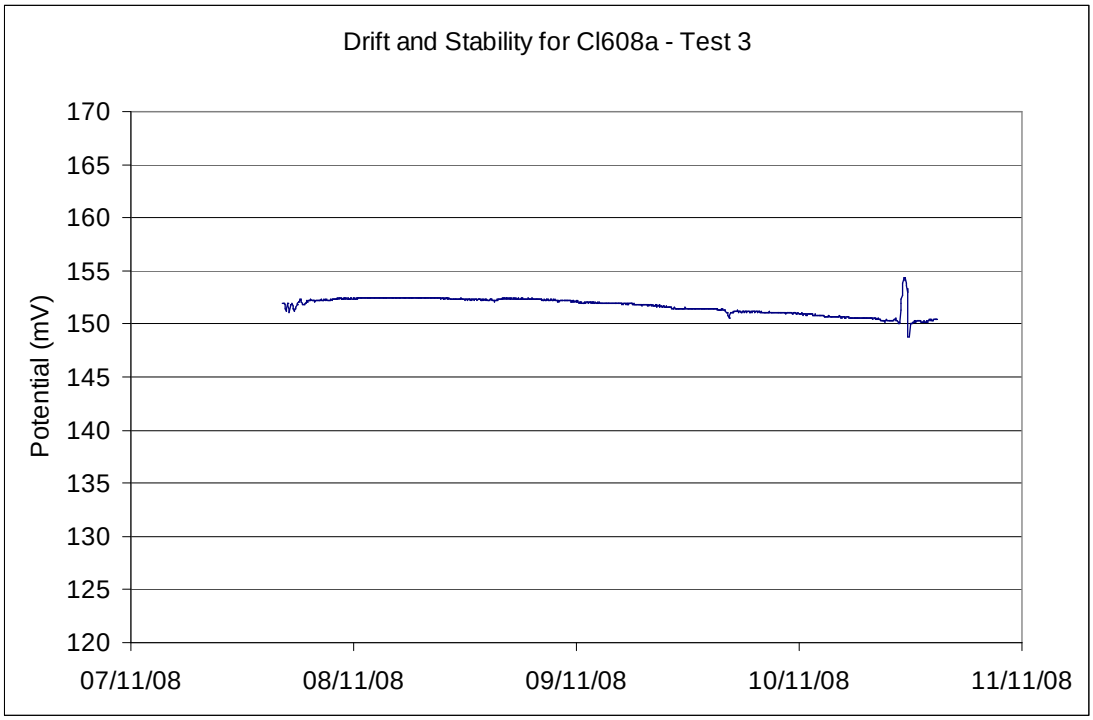
A2. Plots of laboratory tests conducted on the chloride sensors, corresponding to the tests listed in Table 2 of Chapter 3.

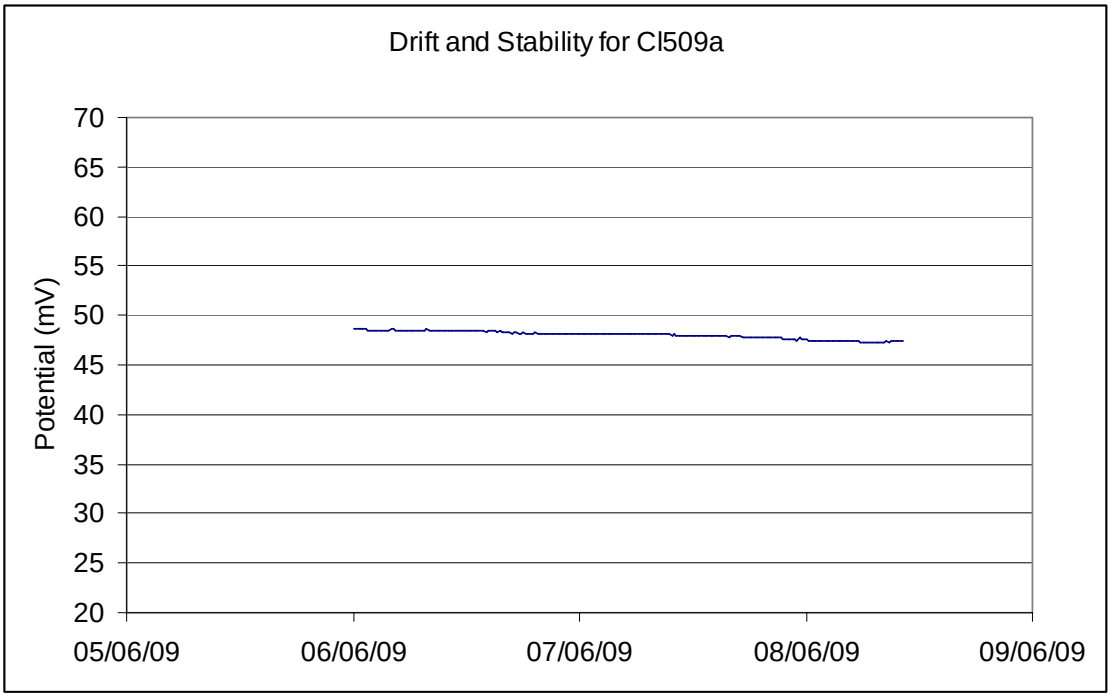


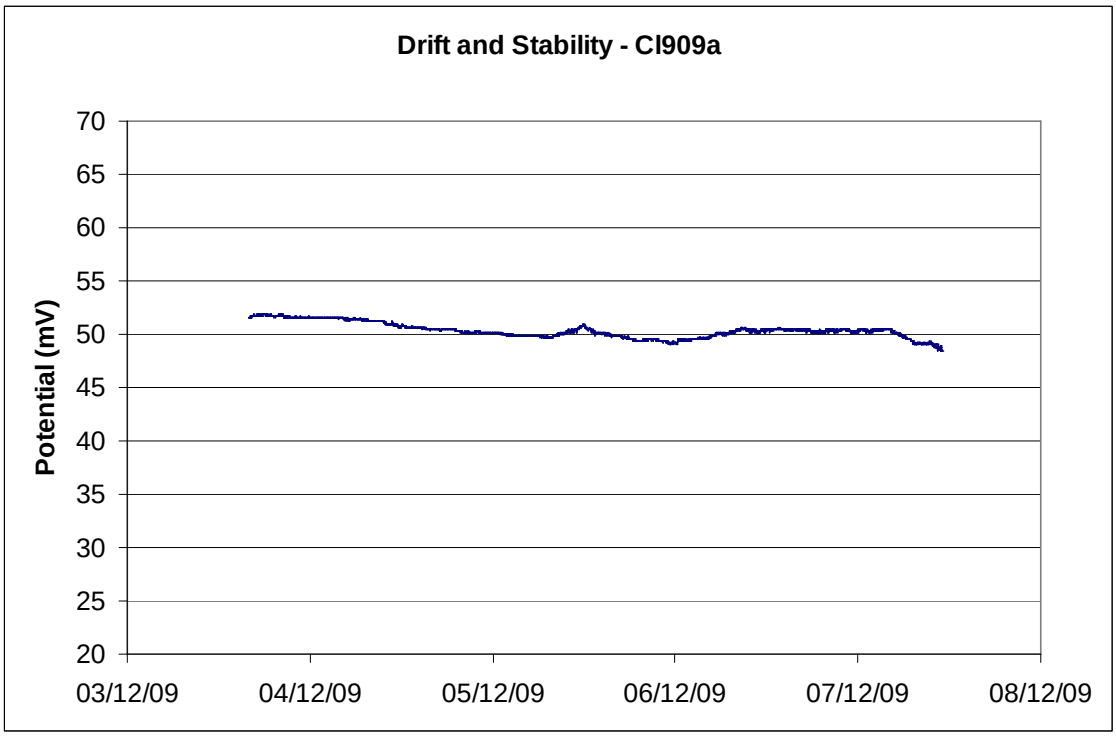



Stability and Drift for Sensor Cl608a - Test 1
Potential (mV)
170
165
160
155
150
145
140
135
130
125
120
09/07/08
11/07/08
13/07/08
15/07/08
17/07/08


Drift and Stability for Cl608a - Test 2
Potential (mV)
140
135
130
125
120
115
110
105
100
95
90
21/07/08
23/07/08
25/07/08
27/07/08
29/07/08
31/07/08
02/08/08
04/08/08
06/08/08


Drift and Stability for Cl608a - Test 3
Potential (mV)
170
165
160
155
150
145
140
135
130
125
120
07/11/08
08/11/08
09/11/08
10/11/08
11/11/08

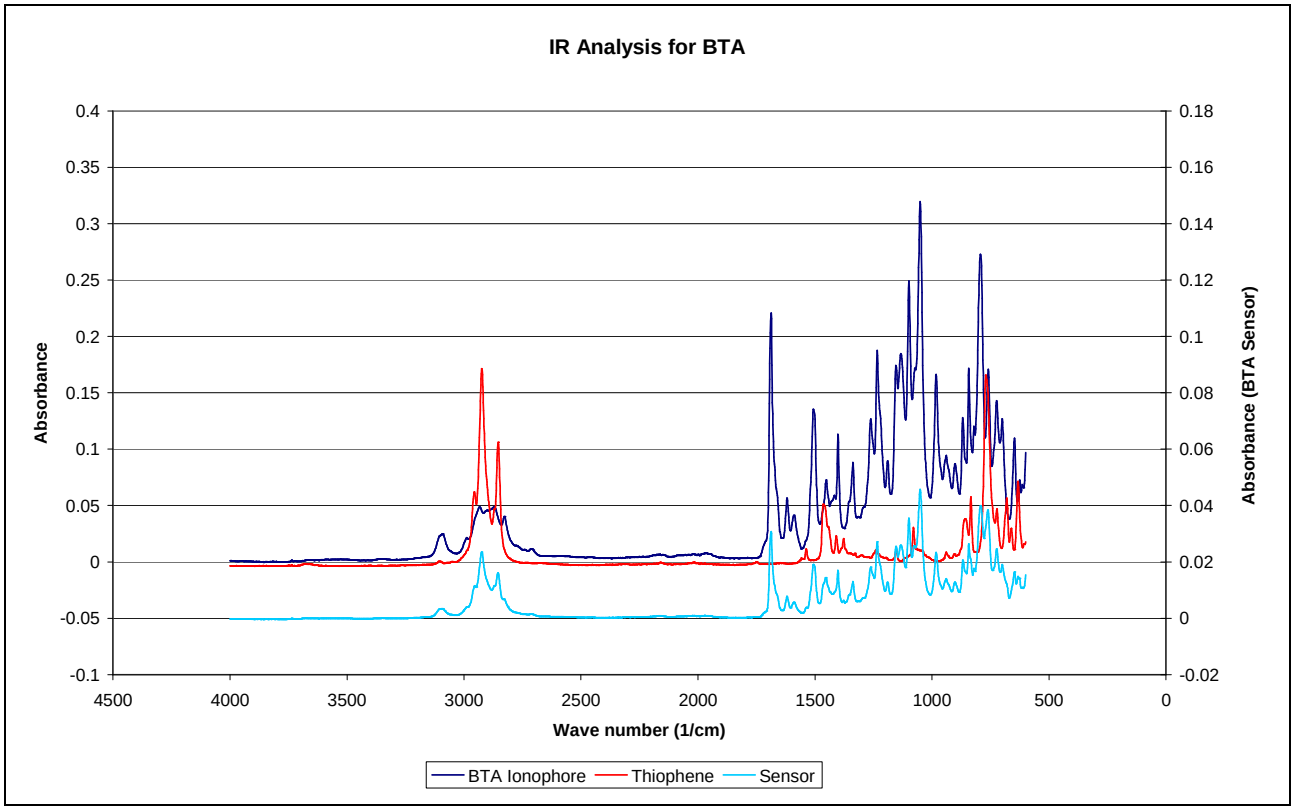

Drift and Stability for Cl509a
Potential (mV)
70
65
60
55
50
45
40
35
30
25
20
05/06/09
06/06/09
07/06/09
08/06/09
09/06/09


Drift and Stability - Cl909a
Potential (mV)
70
65
60
55
50
45
40
35
30
25
20
03/12/09
04/12/09
05/12/09
06/12/09
07/12/09
08/12/09

Appendix B
Sodium Sensor Data

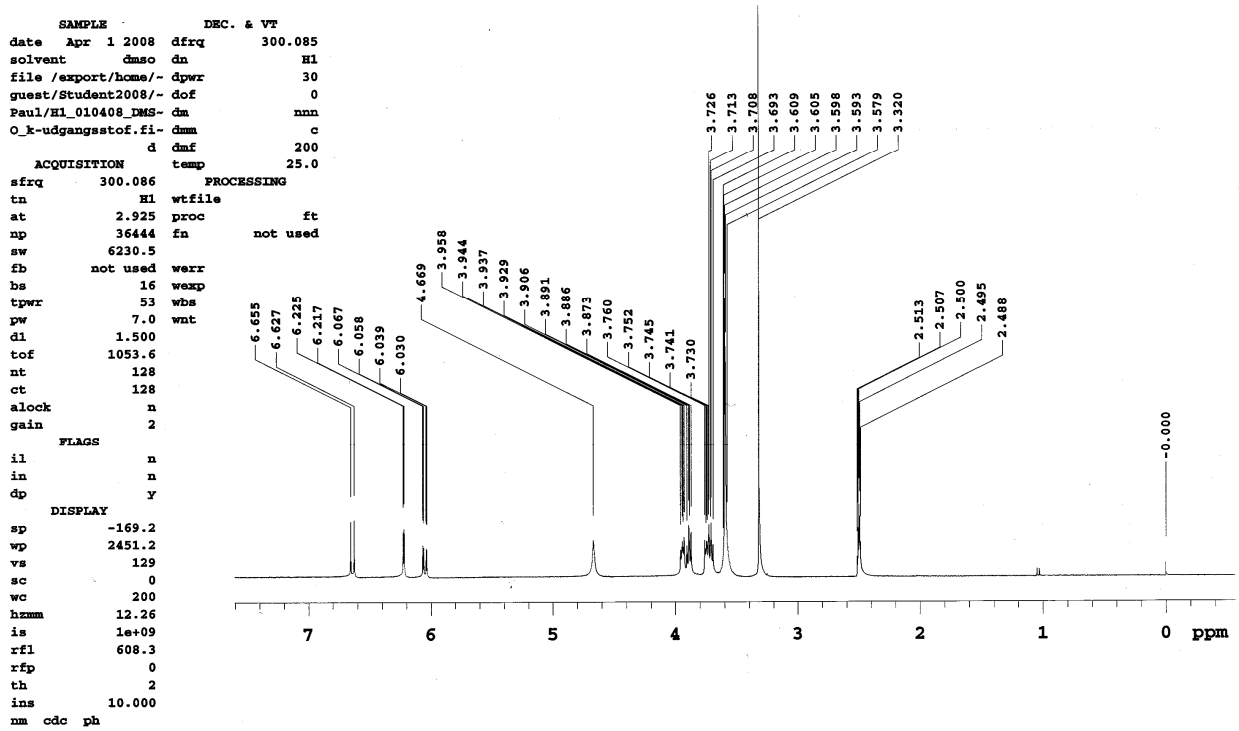
B1. BTA Sensor Series

B1.1 –Infrared absorbance data for the BTA sensors.

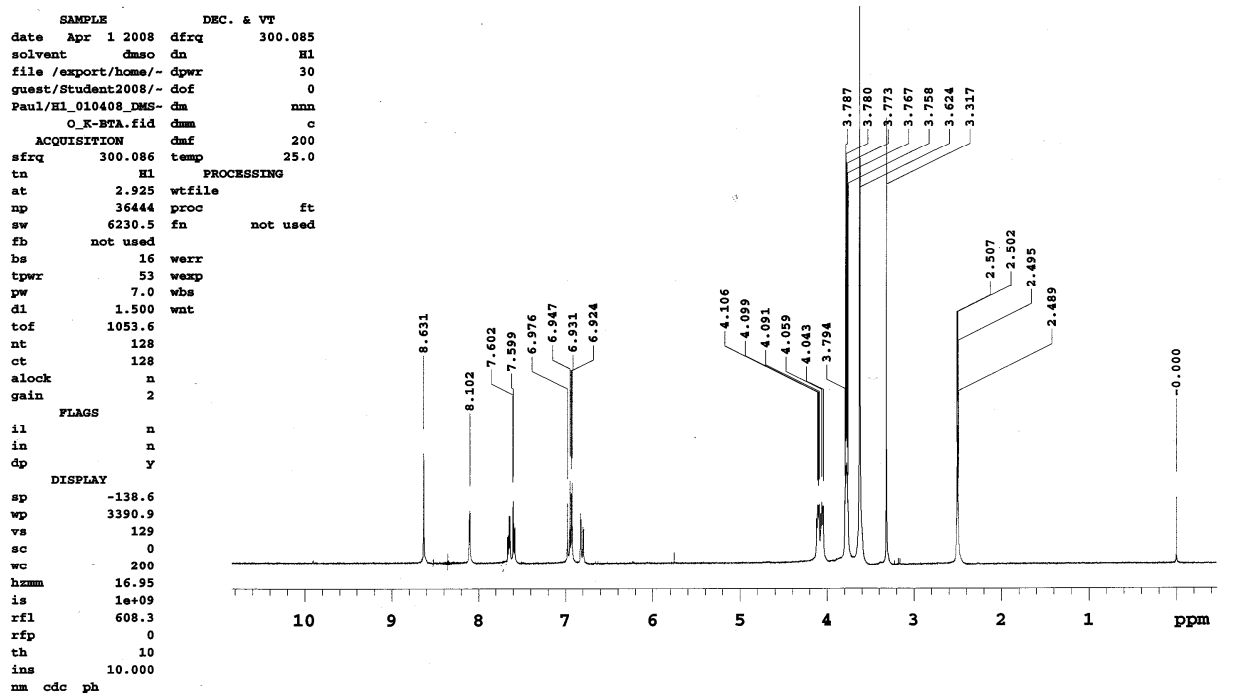


Infrared absorbance data for the BTA sensor (light blue), where the ionophore and thiophene has been co-polymerized on the gold electrode. For reference, there is also infrared absorbance data for the ionophore (dark blue) and thiophene (red) before polymerisation. From the data, it is apparent that the sensor has predominately the signal of the BTA ionophore, indicating that the ionophore was successfully attached to the gold surface.

B1.2 – NMR data for the BTA sensors.

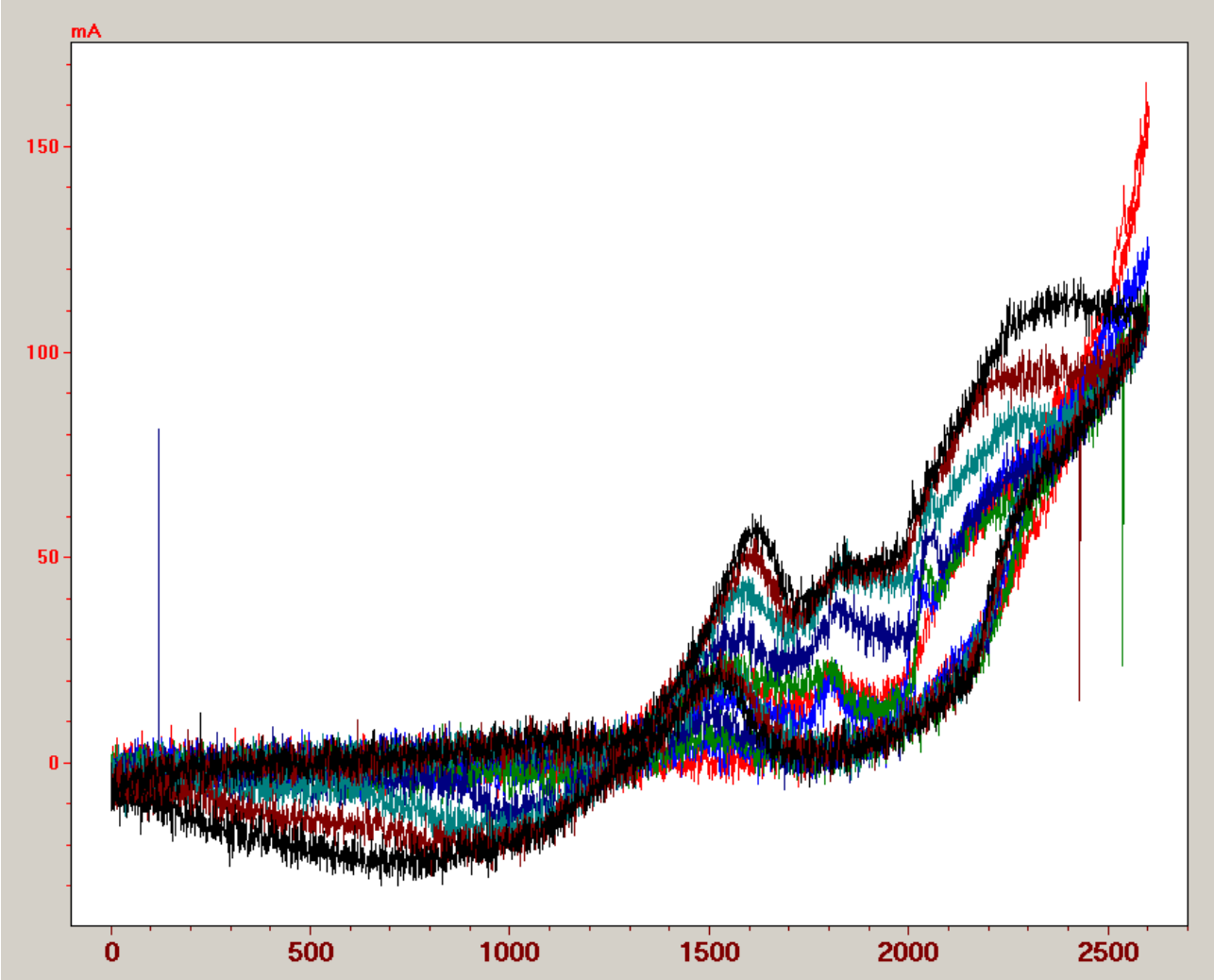


NMR spectra of the original reagent, 4-aminobenzo-15-crown-5, before the cobbling of the thiophene group to form the BTA ionophore.



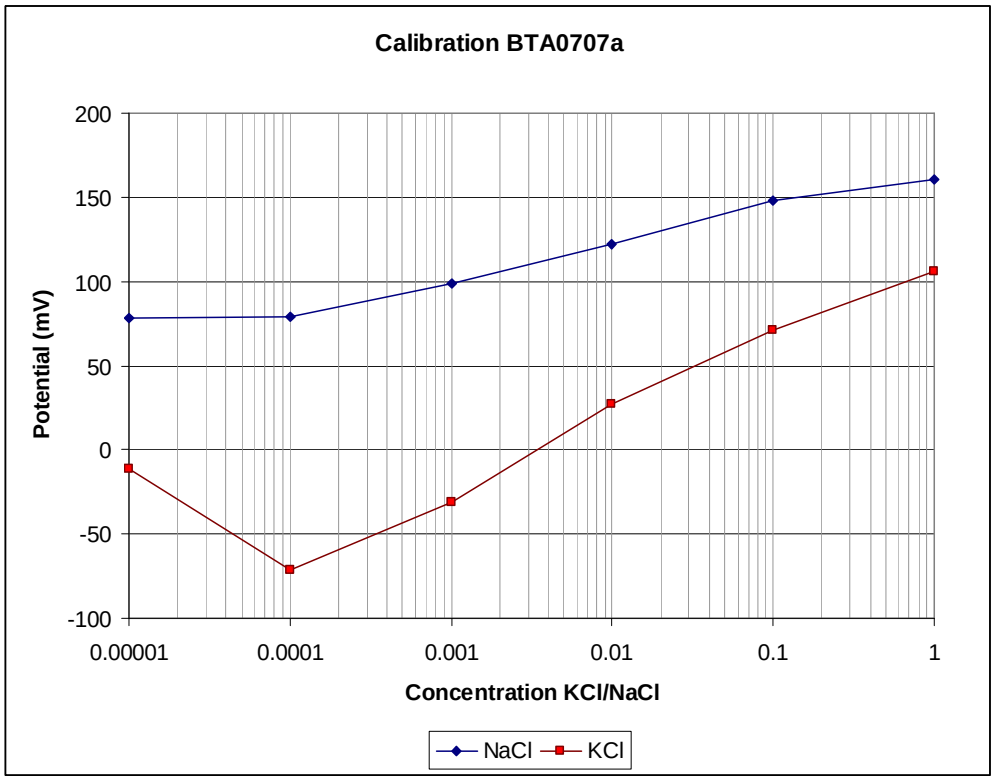
NMR spectra of the BTA ionophore. Note how the hydrogen peaks from the original reagent moved from between 6 and 7ppm to between 6.9 and 7.8ppm, showing that the reaction went to completion.

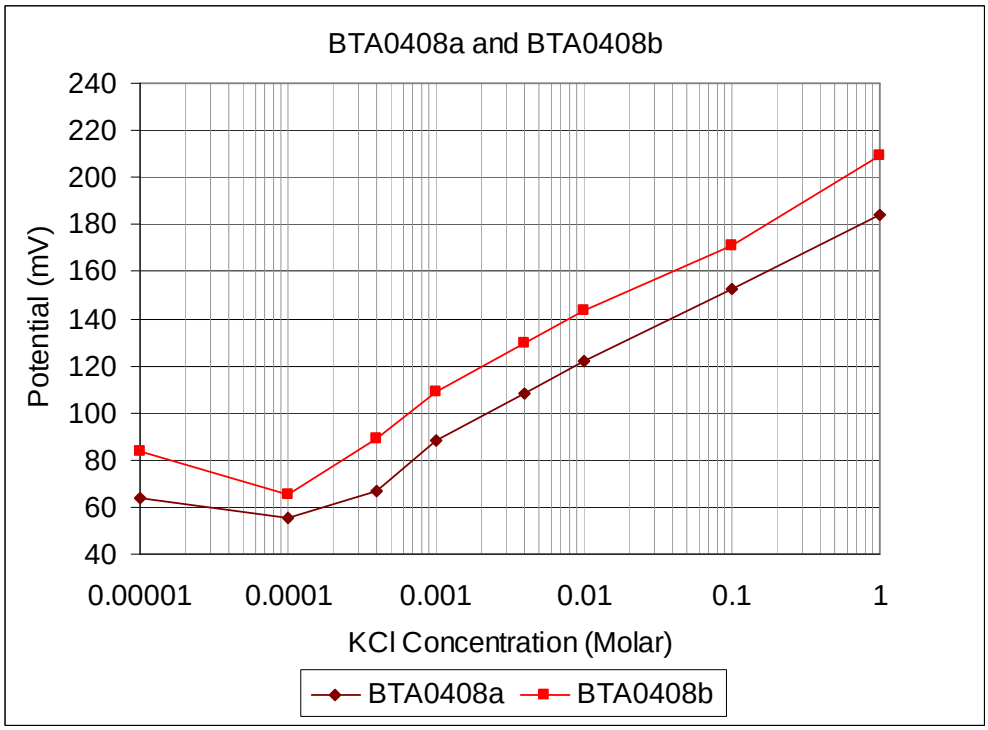
B1.3 Voltammogram showing the co-polymerization of the BTA ionophore

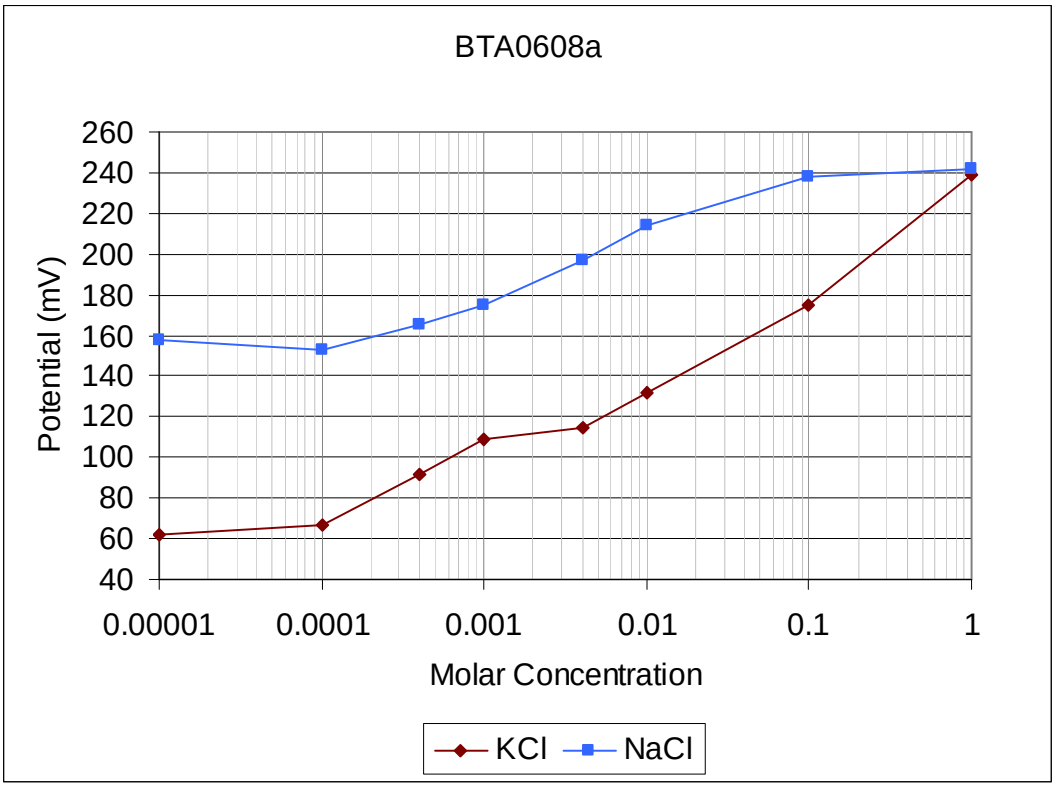


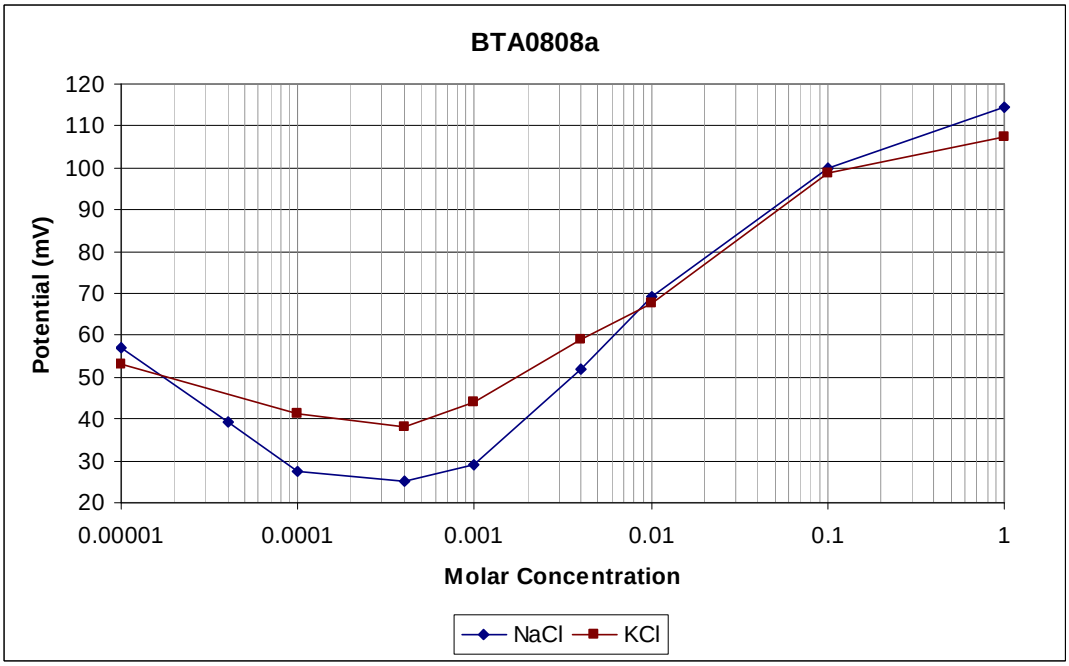
The voltammogram (current in mA vs. potential in mV) of the cyclic voltammetry used to co-polymerize thiophene and the BTA, where the potential (x-axis) was increased at a rate of 10mV/sec from 0-2600mV and then back again. The seven cycles are in order red, blue, green, dark blue, light blue, maroon then black. The measured current (y-axis) is always seen to be higher as the potential increases, and then lower as the potential is decreased back to 0mV. The first peak at approximately 1500-1600mV represents the polymerization of thiophene to thiophene, where as the last peak, at 2600mV represents the polymerization of the thiophene to the BTA. The polymerization process as the potential increases represents the reduction of thiophene and the ionophore forming the thiophene-BTA co-polymer. However, lack of corresponding negative peaks in current on the return cycle show that the polymers were not oxidized again on the return run, and thus that the co-polymerization process is irreversible – thiophene and BTA remain attached to each other. During this process, the sulphur ions in the thiophene become bound to the gold electrode surface, thus producing a solid-state ion selective electrode.

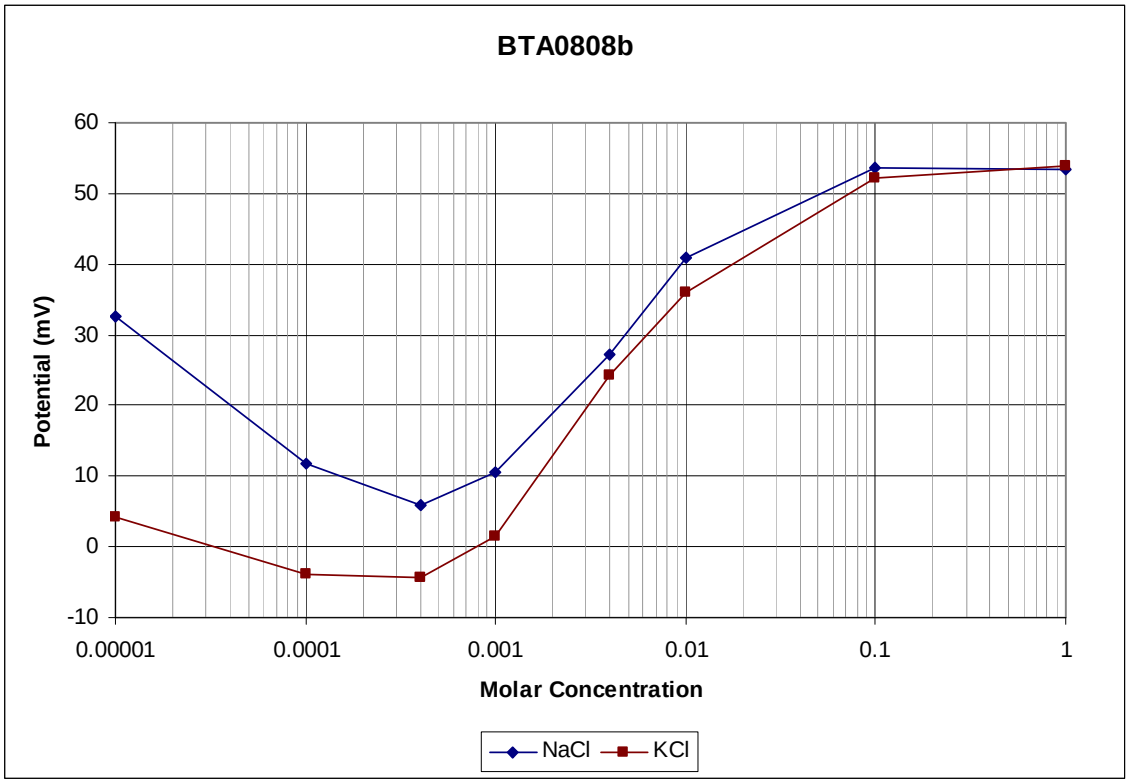
B1.4 Sensor Calibration data for the BTA sensor series, as provided in Table 1, Chapter 4.

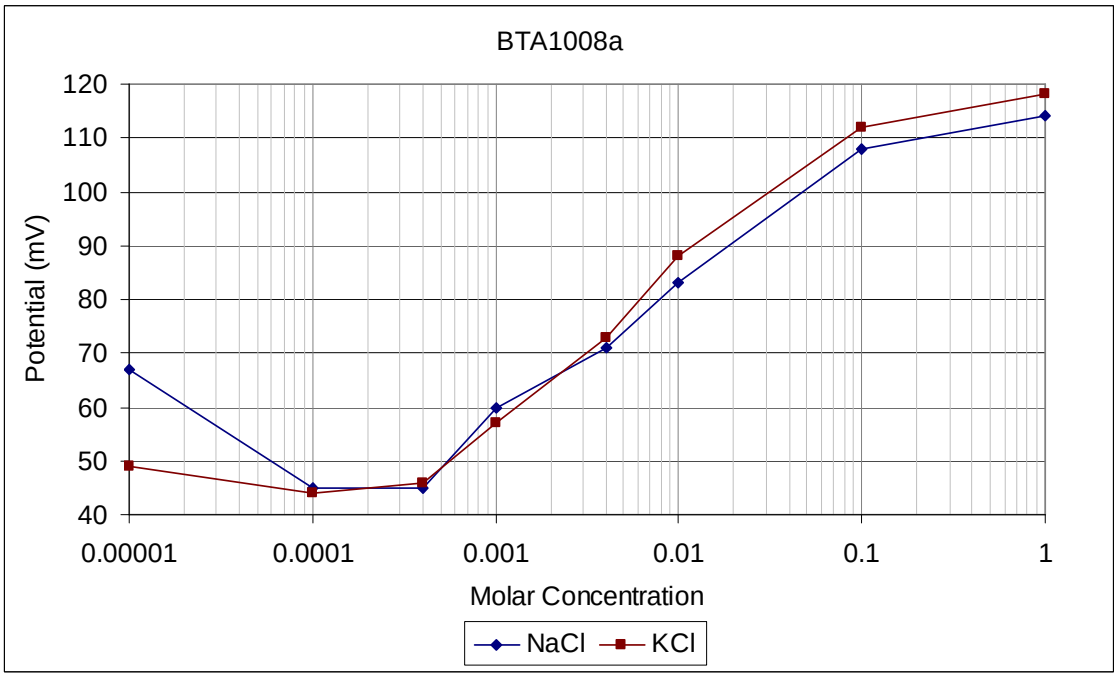


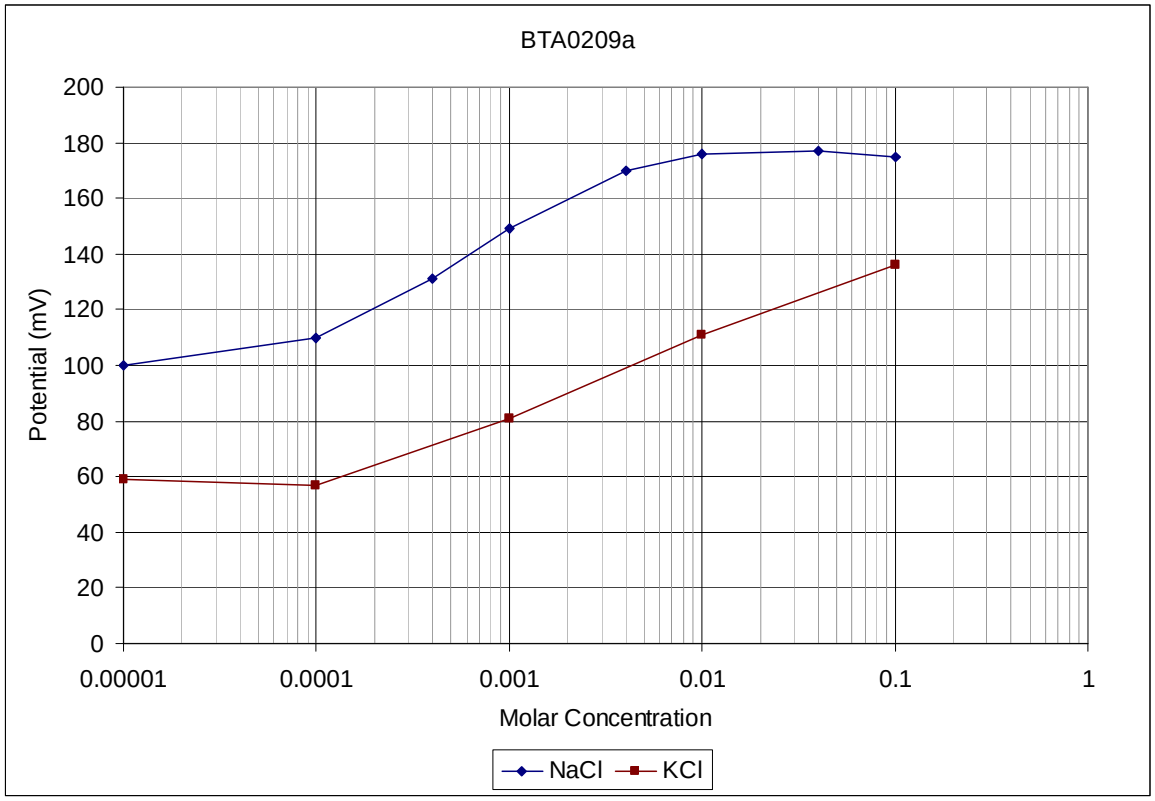


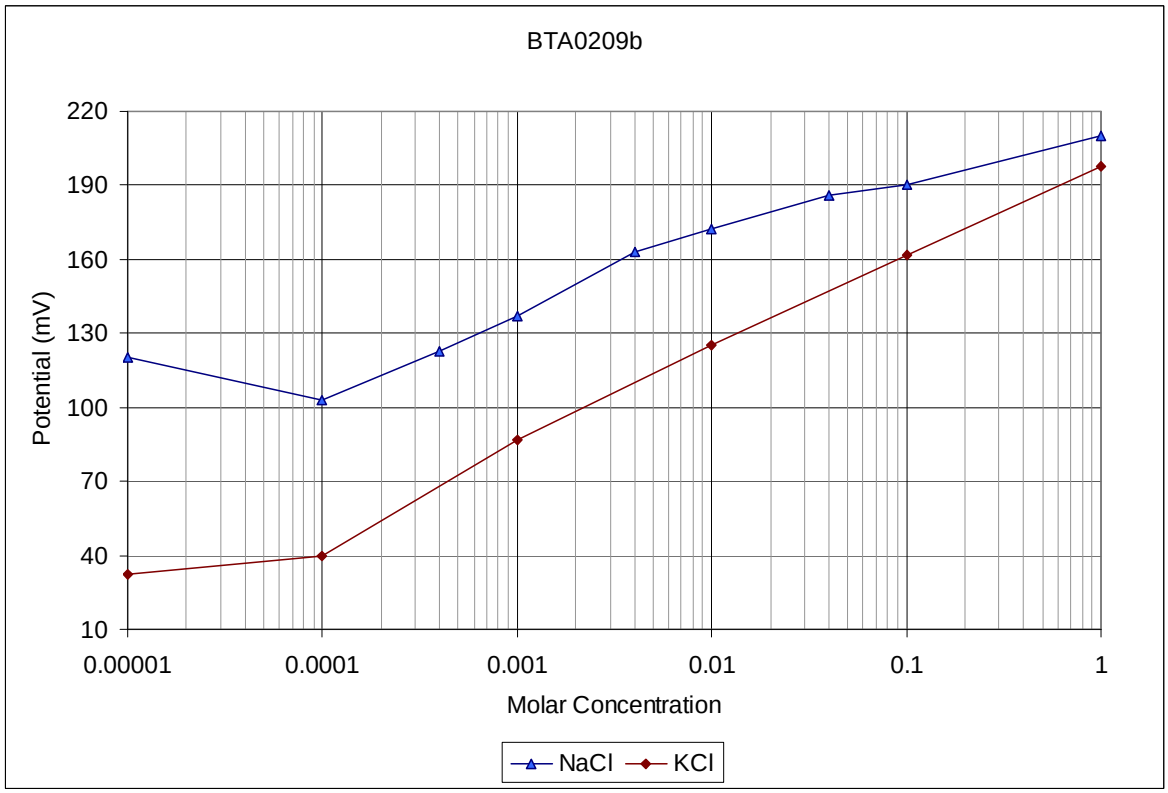

BTA0608a
260
240
220
200
180
160
140
120
100
80
60
40
Potential (mV)
0.00001
0.0001
0.001
0.01
0.1
1
Molar Concentration
KCl
NaCl

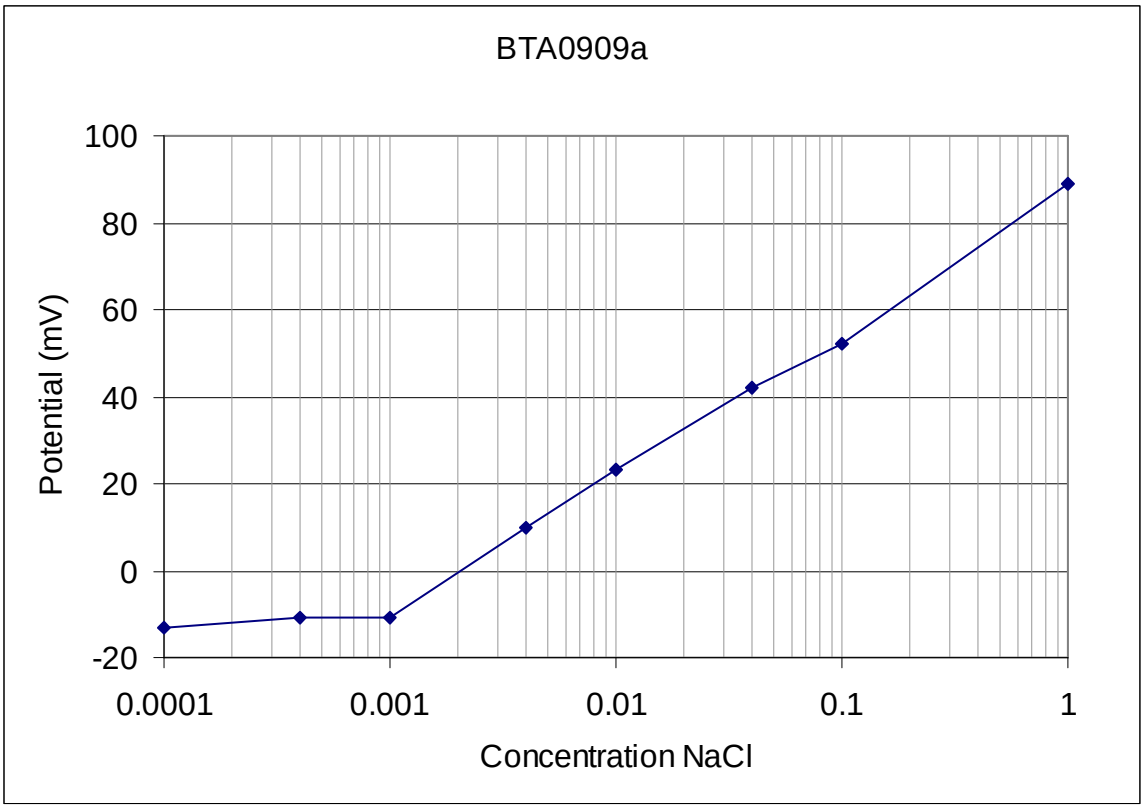

BTA0808a
120
110
100
90
80
70
60
50
40
30
20
Potential (mV)
0.00001
0.0001
0.001
0.01
0.1
1
Molar Concentration
NaCl
KCl


BTA0808b
60
50
40
30
20
10
0
-10
Potential (mV)
0.00001
0.0001
0.001
0.01
0.1
1
Molar Concentration
NaCl
KCl

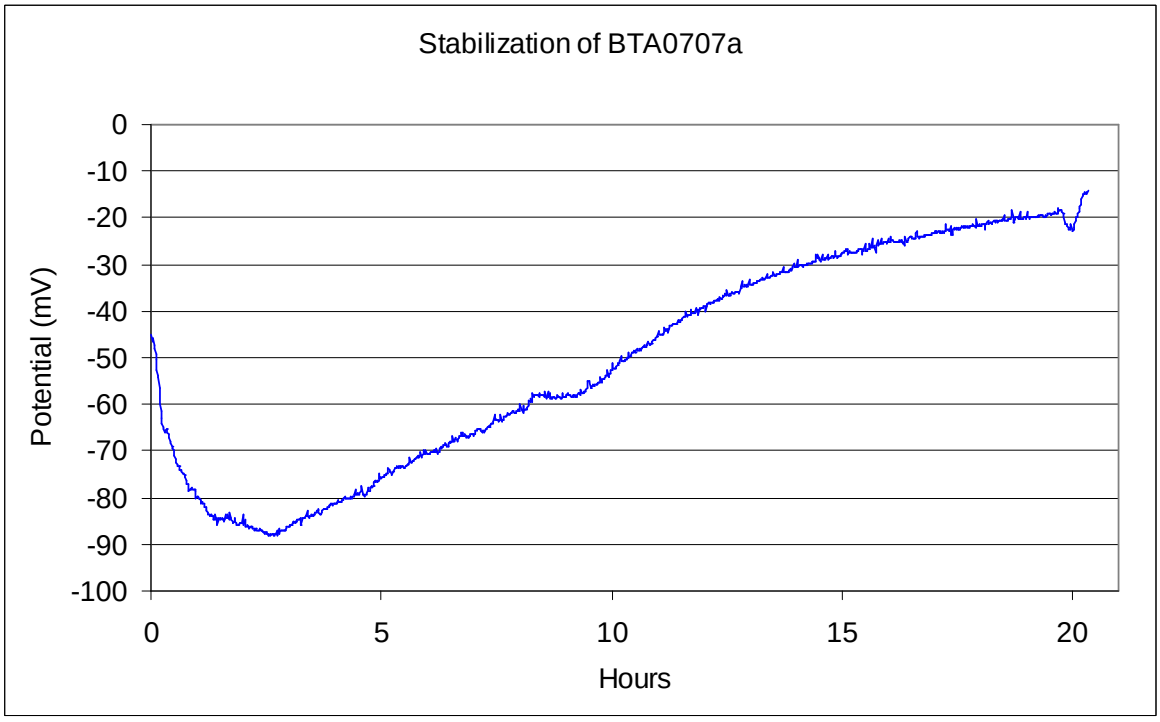

BTA1008a
120
110
100
90
80
70
60
50
40
Potential (mV)
0.00001
0.0001
0.001
0.01
0.1
1
Molar Concentration
NaCl
KCl

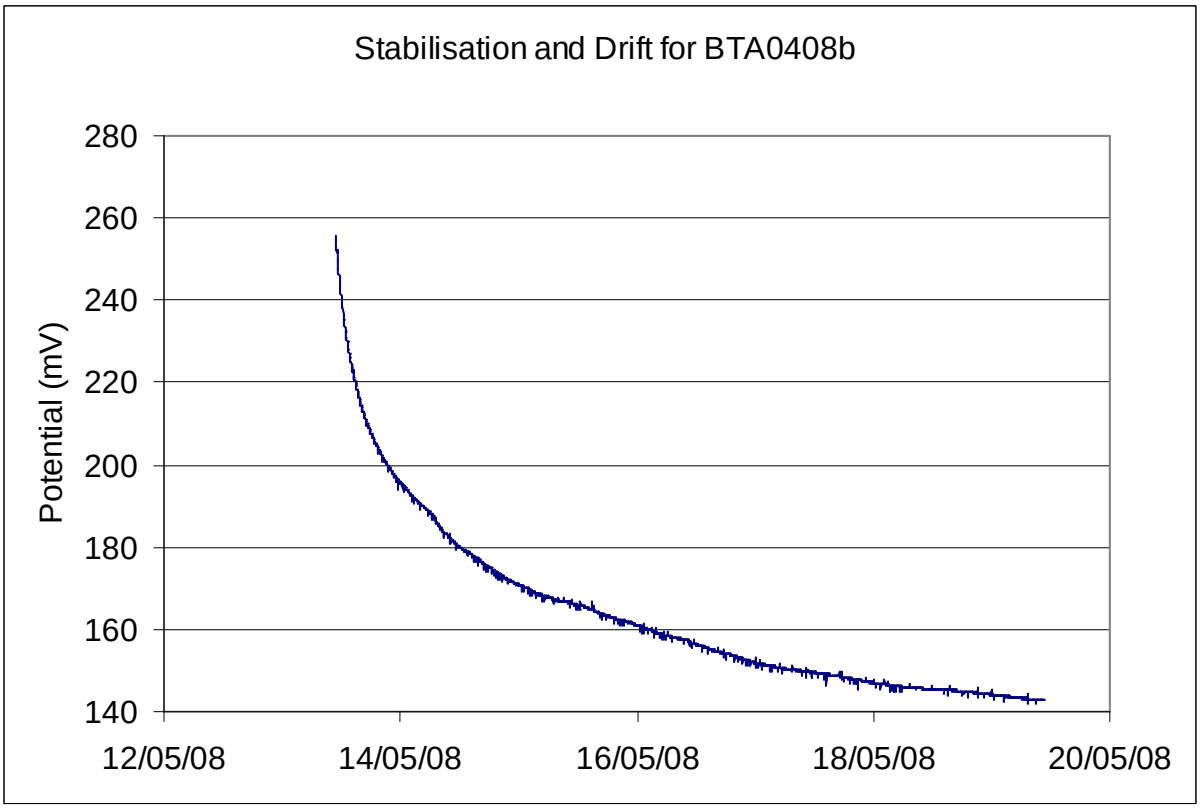

BTA0209a
Potential (mV)
200
180
160
140
120
100
80
60
40
20
0
0.00001
0.0001
0.001
0.01
0.1
1
Molar Concentration
NaCl
KCl

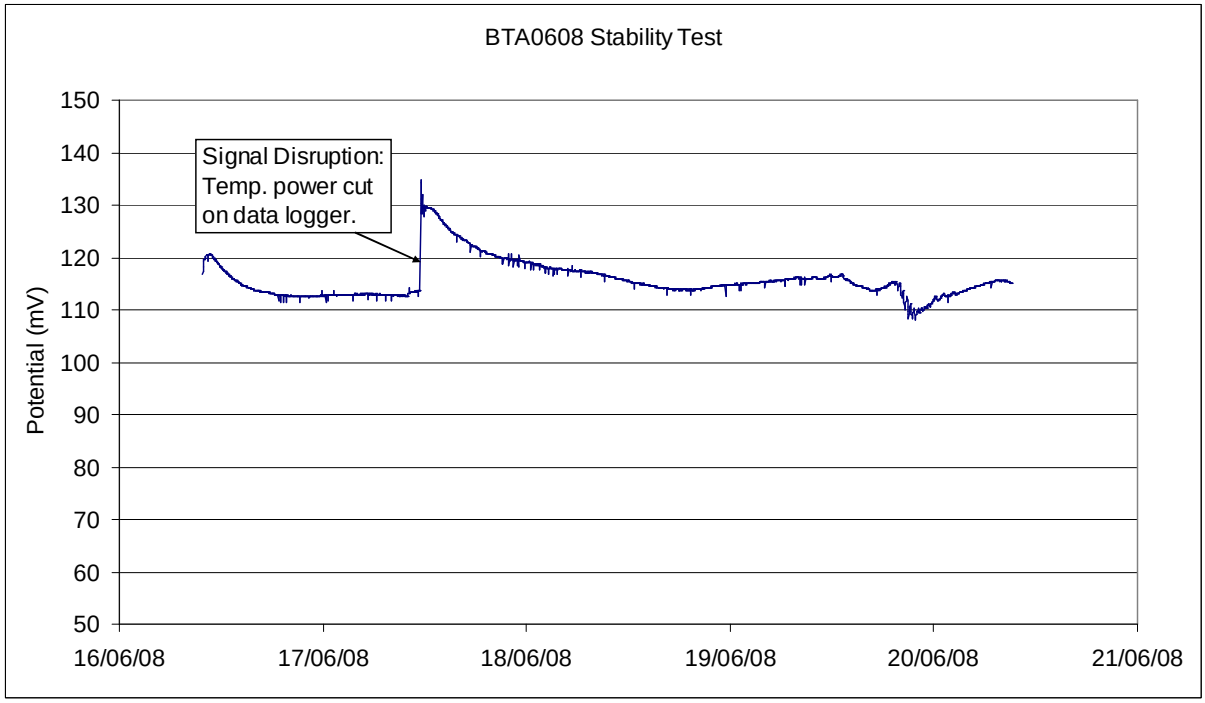

BTA0209b
Potential (mV)
220
190
160
130
100
70
40
10
0.00001
0.0001
0.001
0.01
0.1
1
Molar Concentration
NaCl
KCl

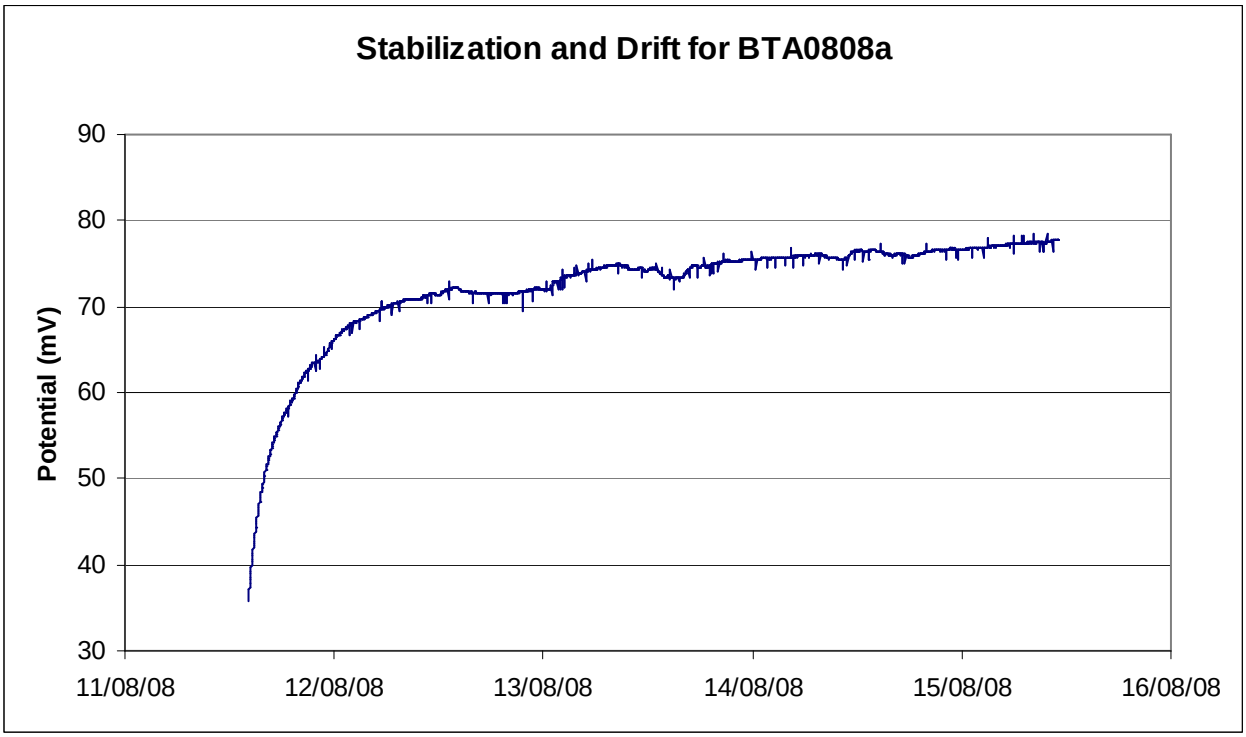


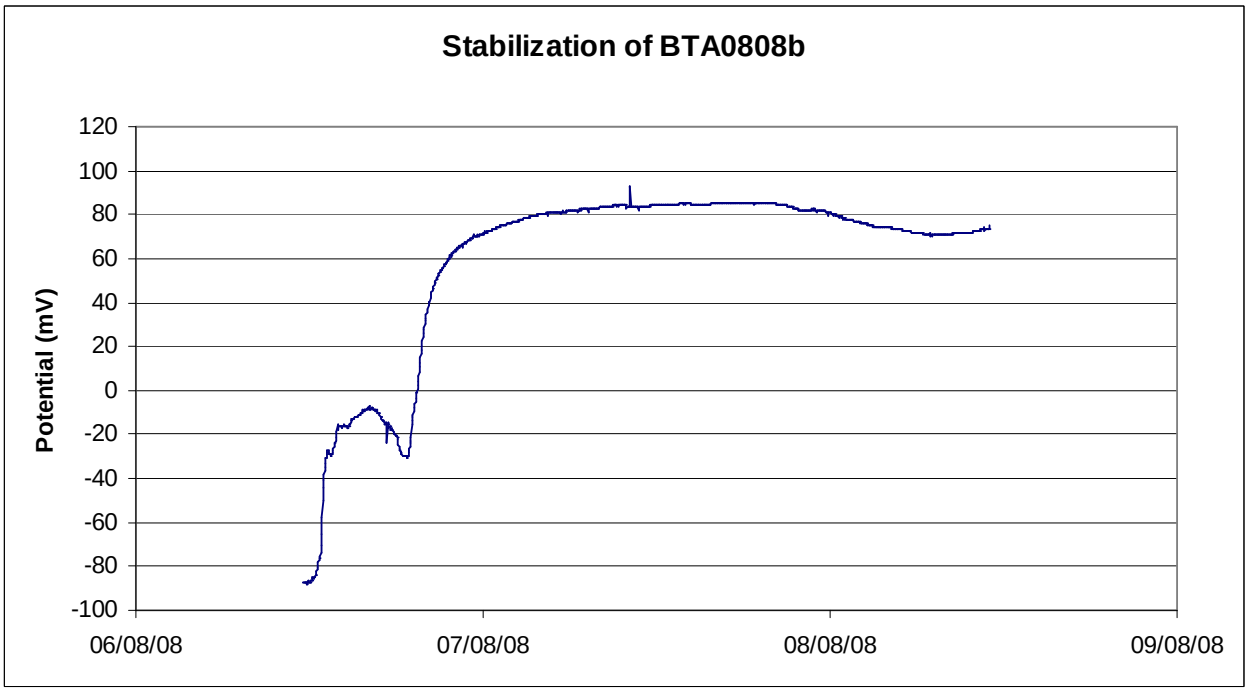
B1.5 Stabilization data for the BTA sensors where long-term testing was conducted.




Stabilisation and Drift for BTA0408b
Potential (mV)
280
260
240
220
200
180
160
140
12/05/08
14/05/08
16/05/08
18/05/08
20/05/08

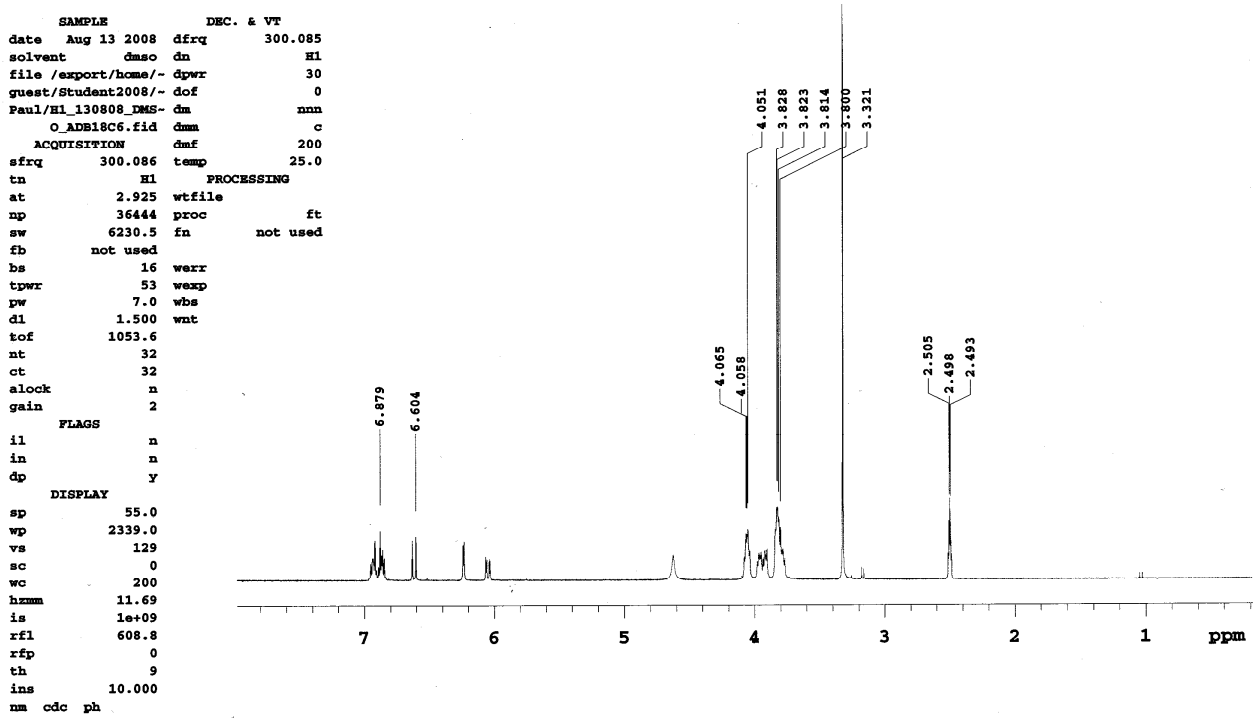

BTA0608 Stability Test
Potential (mV)
150
140
130
120
110
100
90
80
70
60
50
Signal Disruption:
Temp. power cut
on data logger.
16/06/08
17/06/08
18/06/08
19/06/08
20/06/08
21/06/08


Stabilization and Drift for BTA0808a
Potential (mV)
90
80
70
60
50
40
30
11/08/08
12/08/08
13/08/08
14/08/08
15/08/08
16/08/08

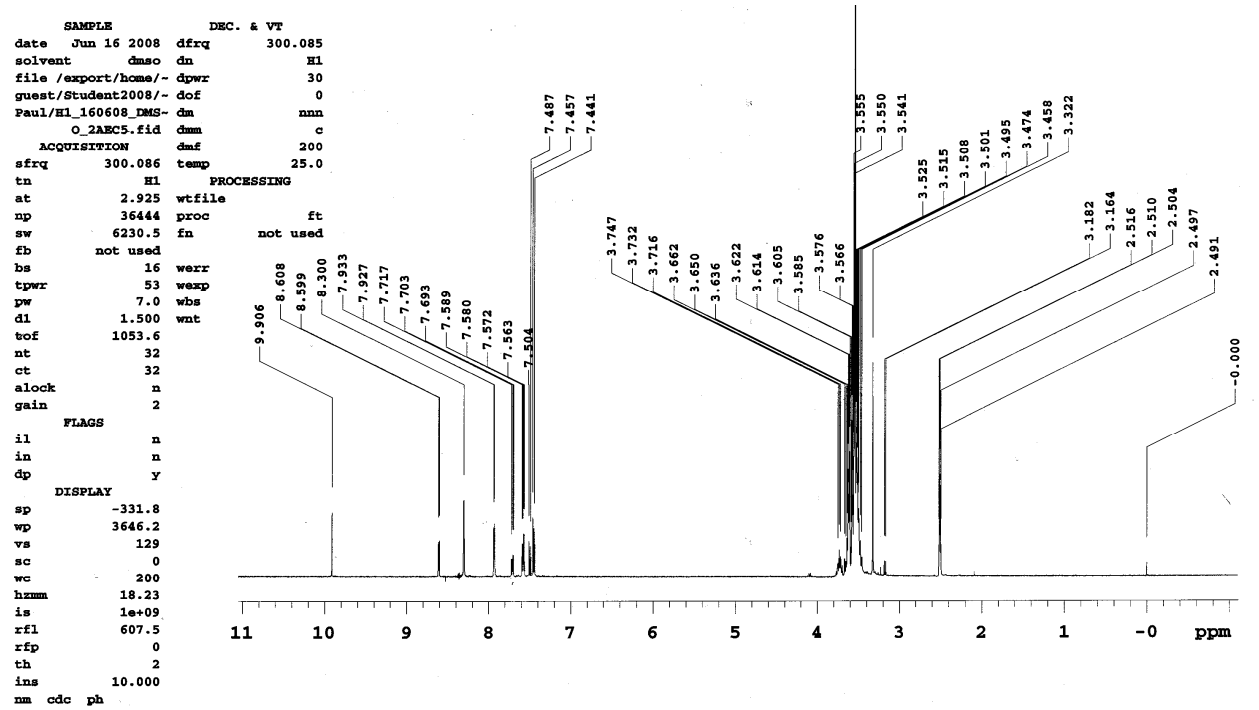

Stabilization of BTA0808b
Potential (mV)
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
06/08/08
07/08/08
08/08/08
09/08/08

B2. MTA Sensor Series

B2.1 NMR Data for the MTA sensors.

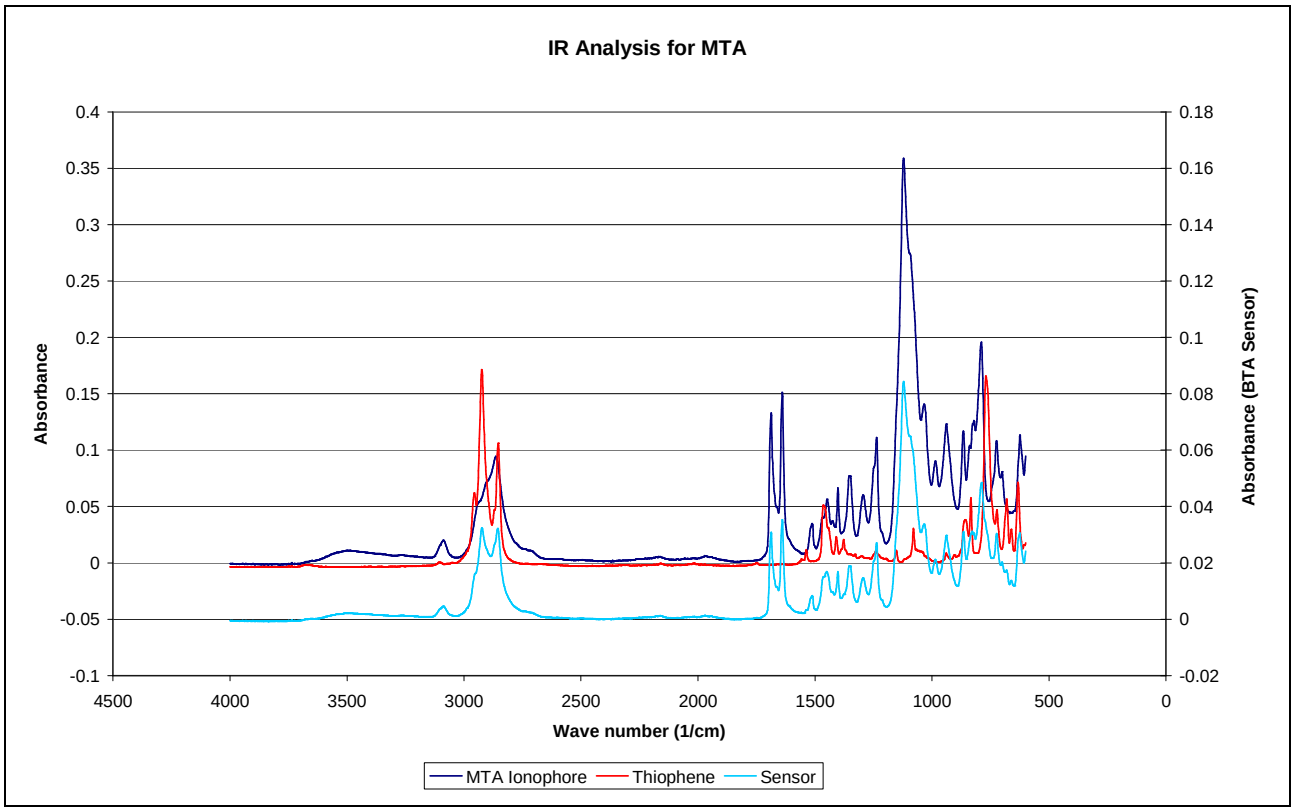


NMR spectra for the original reagent, 2-aminomethyl-15-crown-5, before the cobbling of the thiophene group to the ionophore.



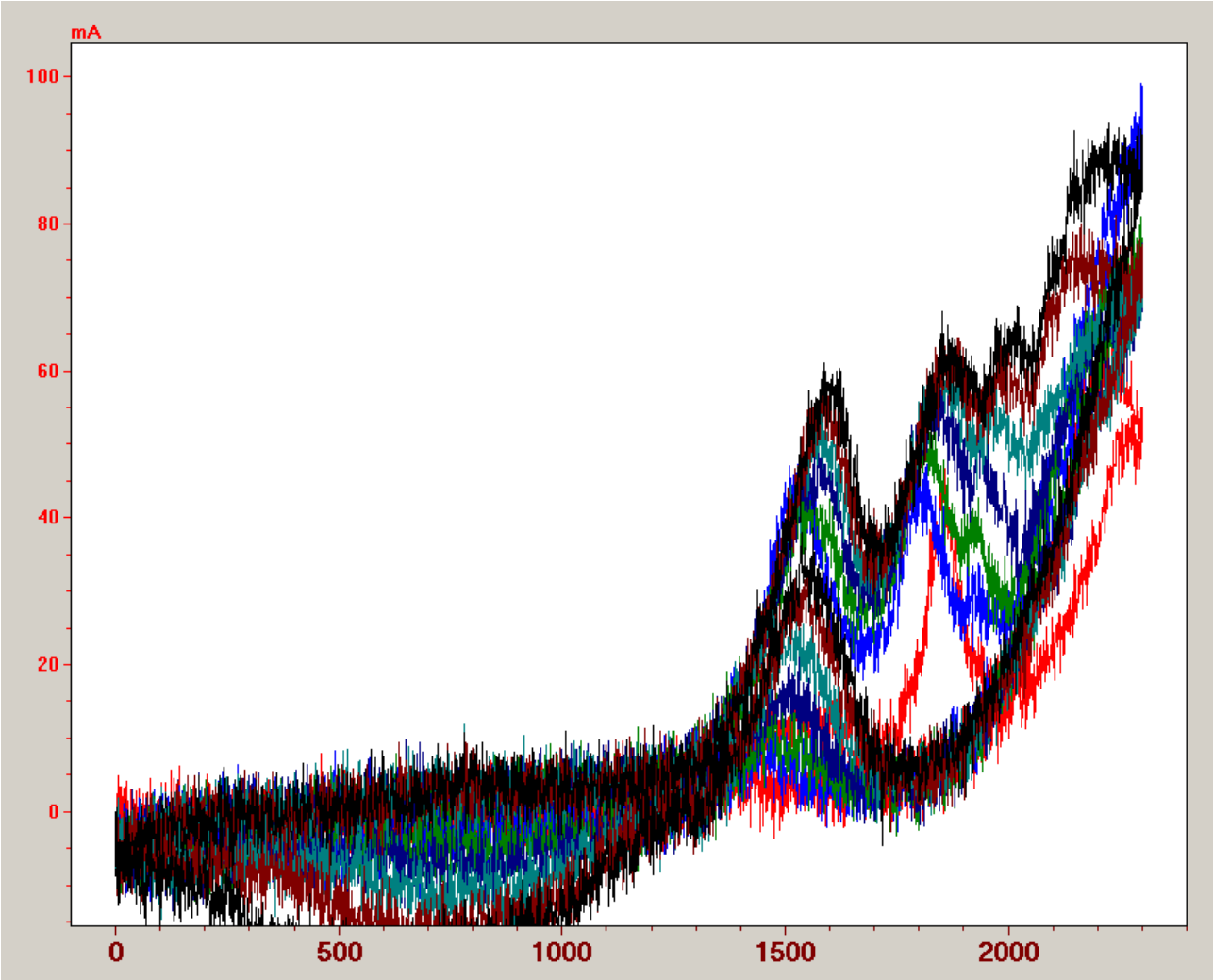
NMR spectra for the MTA ionophore. Note the hydrogen peaks from between 6 and 7ppm in the reagent to between 7.5 and 8.5 in the MTA (product) indicating that the reaction went to completion.

B2.2 Infrared spectra for the MTA sensors



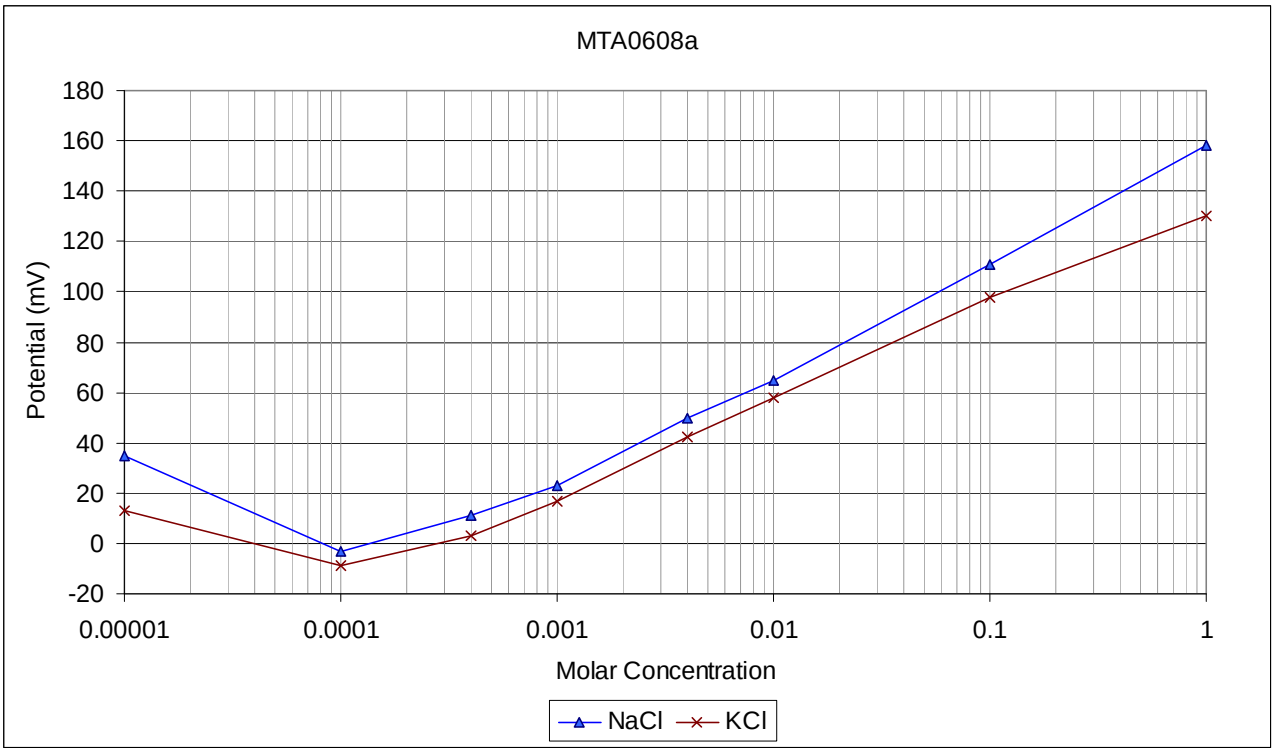
Infrared absorbance data for the MTA sensor (light blue), where the ionophore and thiophene has been co-polymerized on the gold electrode. For reference, there is also infrared absorbance data for the ionophore (dark blue) and thiophene (red) before polymerisation. From the data, it is apparent that the sensor has predominately the signal of the MTA ionophore, indicating that the ionophore was successfully attached to the gold surface.

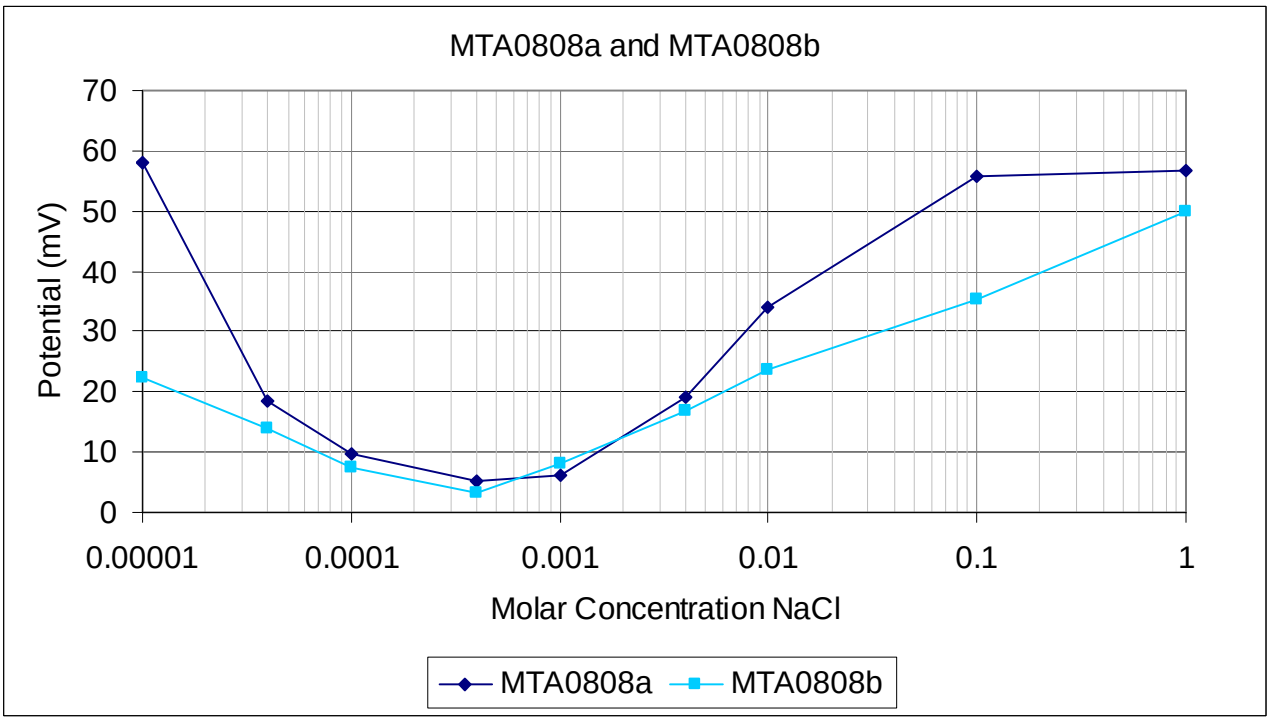
B2.3 Voltammogram showing the co-polymerization of the MTA ionophore

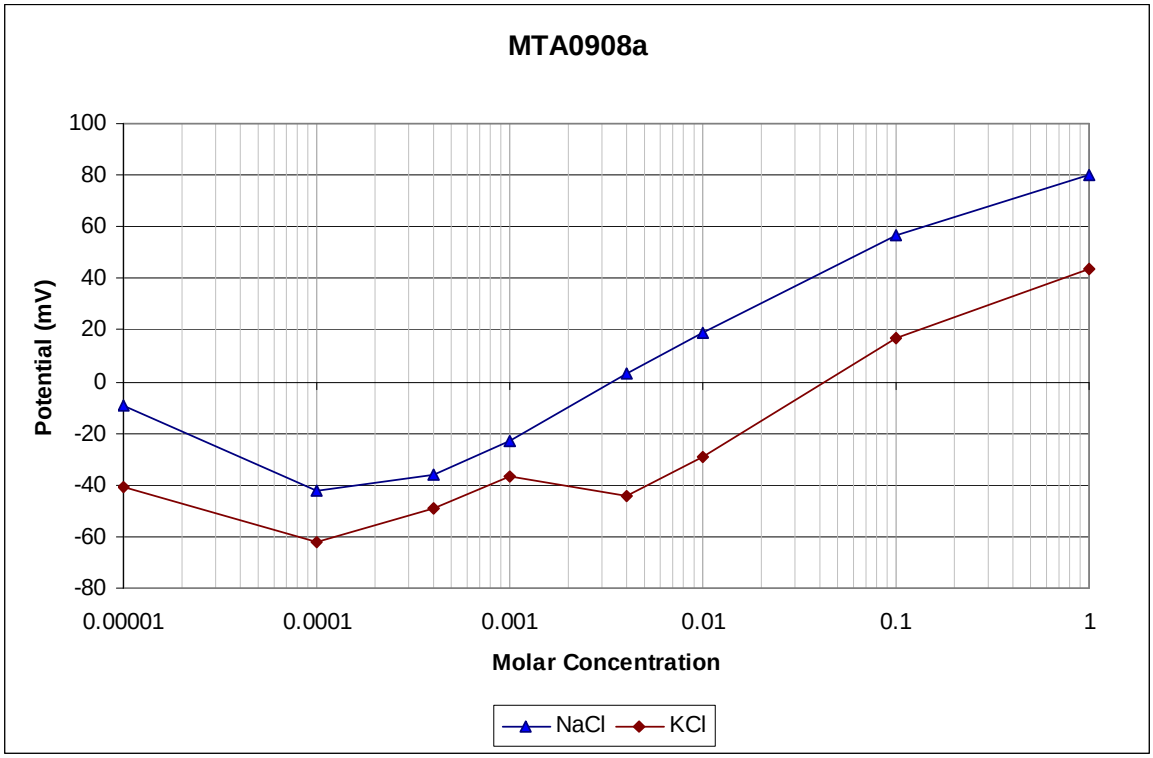


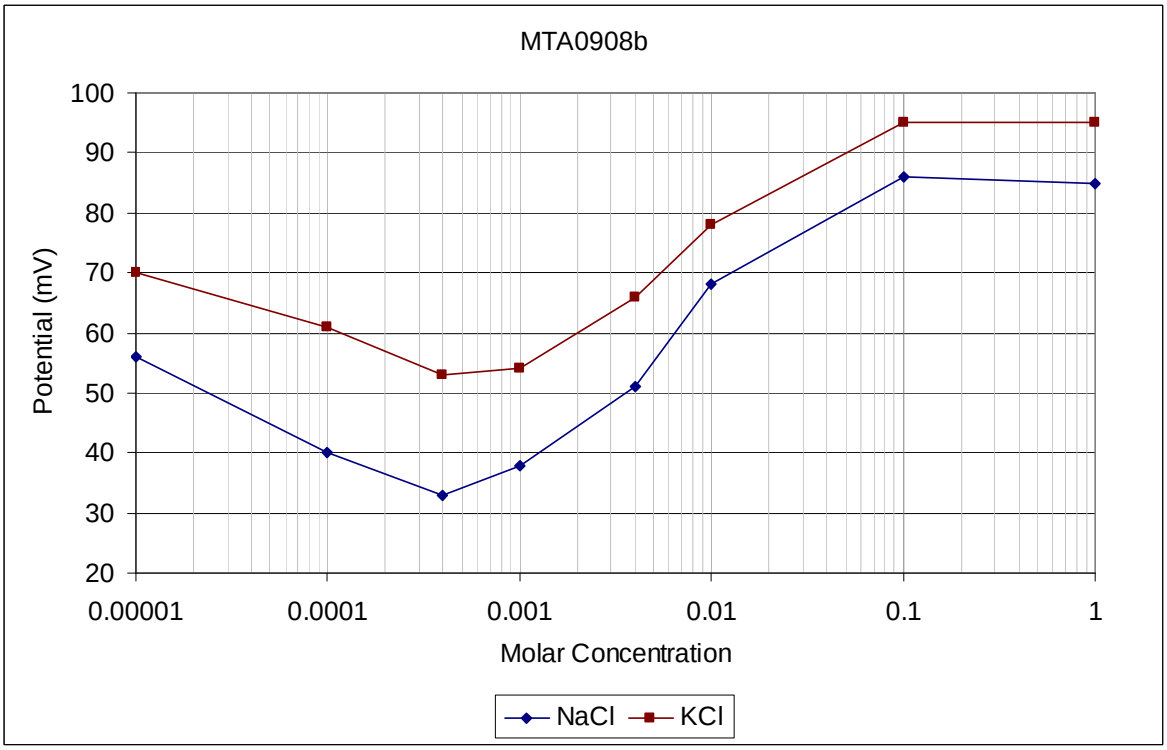
The voltammogram (current in mA vs. potential in mV) of the cyclic voltammetry used to co-polymerize thiophene and the MTA, where the potential (x-axis) was increased at a rate of 10mV/sec from 0-2400mV and then back again. The seven cycles are in order red, blue, green, dark blue, light blue, maroon then black. The measured current (y-axis) is always seen to be higher as the potential increases, and then lower as the potential is decreased back to 0mV. The first peak at approximately 1500-1600mV represents the polymerization of thiophene to thiophene, where as the last peak, at 2400mV represents the polymerization of the thiophene to the MTA. The polymerization process as the potential increases represents the reduction of thiophene and the ionophore forming the thiophene-MTA co-polymer. However, lack of corresponding negative peaks in current on the return cycle show that the polymers were not oxidized again on the return run, and thus that the co-polymerization process is irreversible – thiophene and MTA remain attached to each other. During this process, the sulphur ions in the thiophene become bound to the gold electrode surface, thus producing a solid-state ion selective electrode.

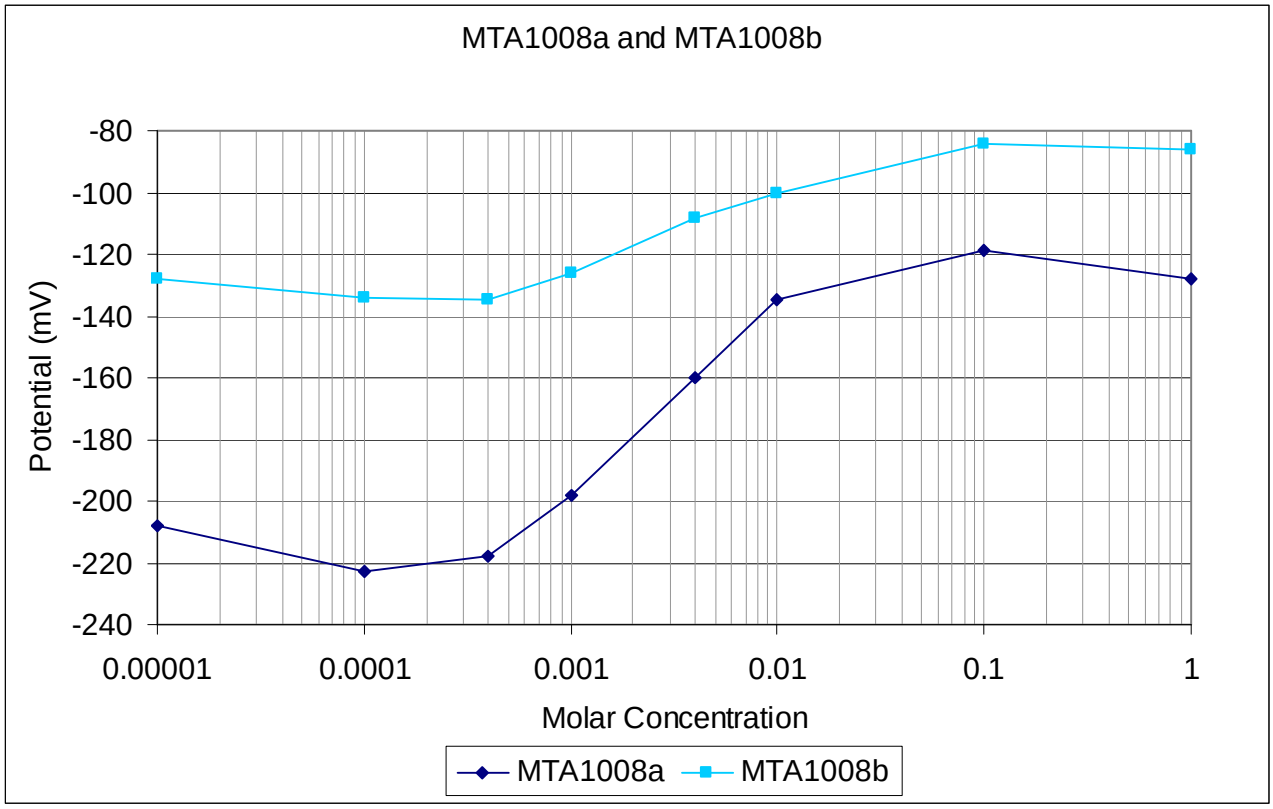
B2.4 Sensor Calibration data for the MTA sensor series, as provided in Table 2, Chapter 4.

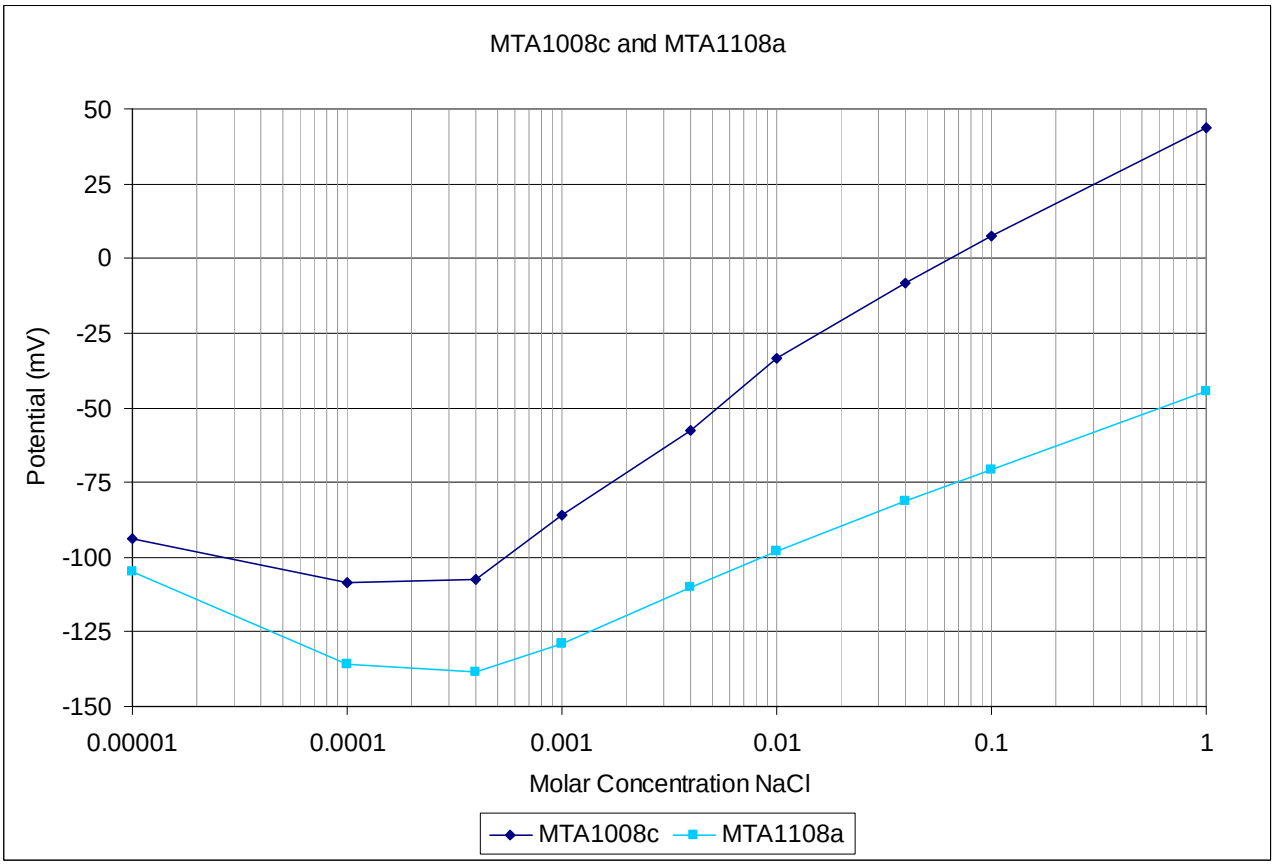


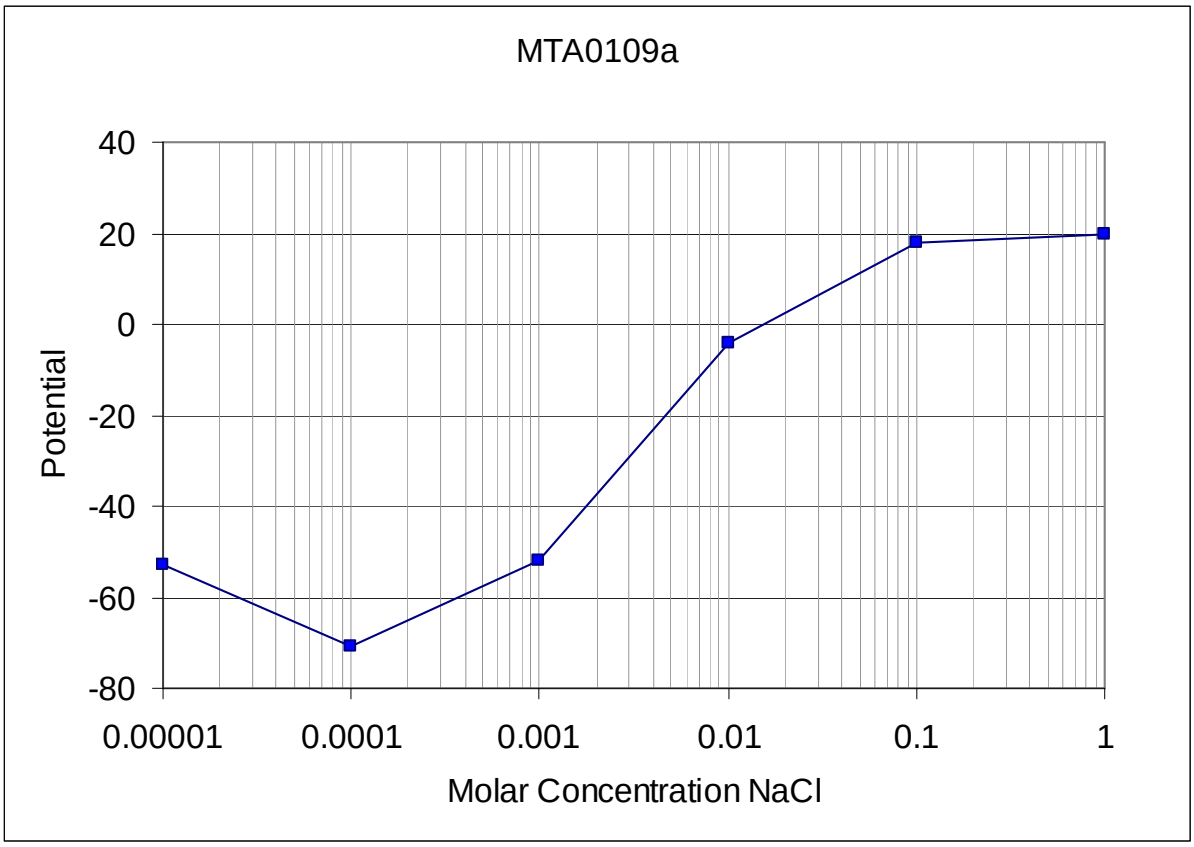


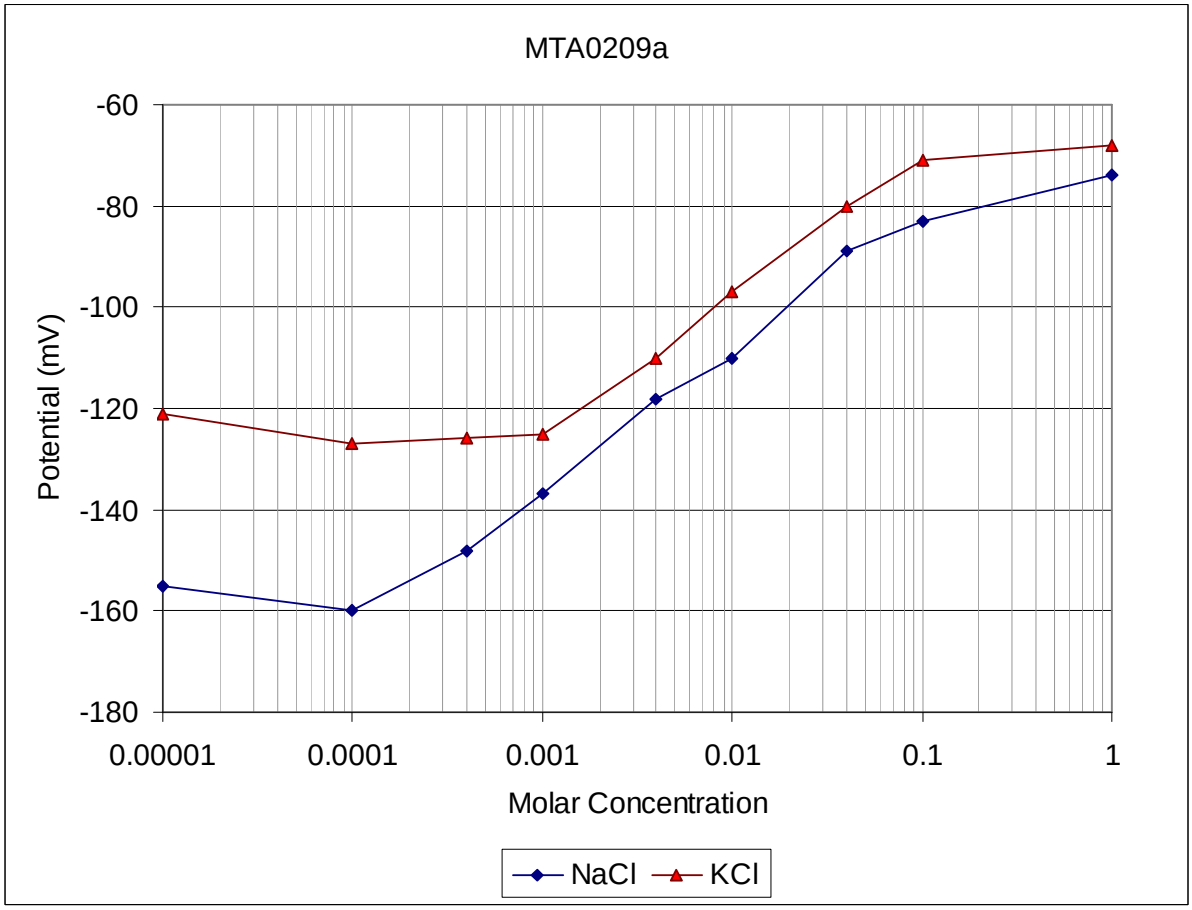

MTA0908a
100
80
60
40
20
0
-20
-40
-60
-80
Potential (mV)
0.00001
0.0001
0.001
0.01
0.1
1
Molar Concentration
NaCl
KCl


MTA0908b
100
90
80
70
60
50
40
30
20
Potential (mV)
0.00001
0.0001
0.001
0.01
0.1
1
Molar Concentration
NaCl
KCl

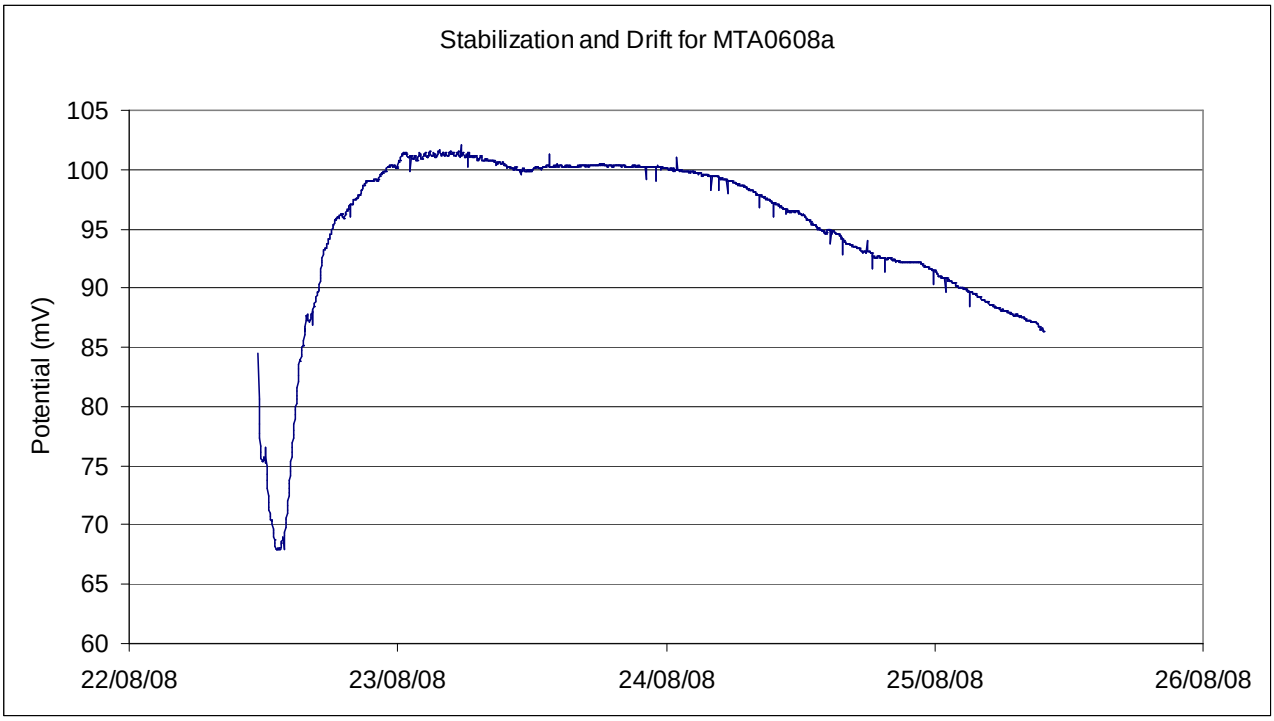

MTA1008a and MTA1008b
-80
-100
-120
-140
-160
-180
-200
-220
-240
Potential (mV)
0.00001
0.0001
0.001
0.01
0.1
1
Molar Concentration
MTA1008a
MTA1008b

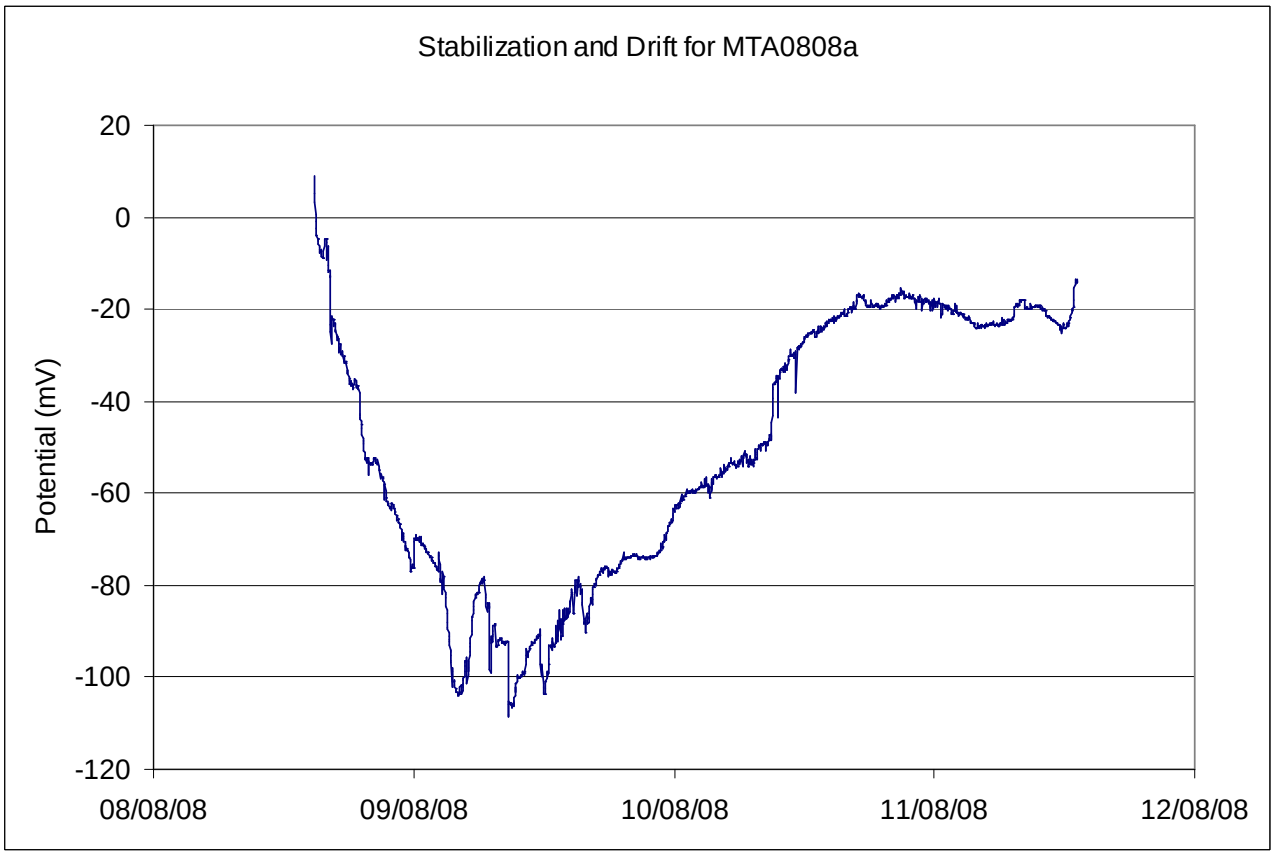

MTA1008c and MTA1108a
50
25
0
-25
-50
-75
-100
-125
-150
Potential (mV)
0.00001
0.0001
0.001
0.01
0.1
1
Molar Concentration NaCl
MTA1008c
MTA1108a

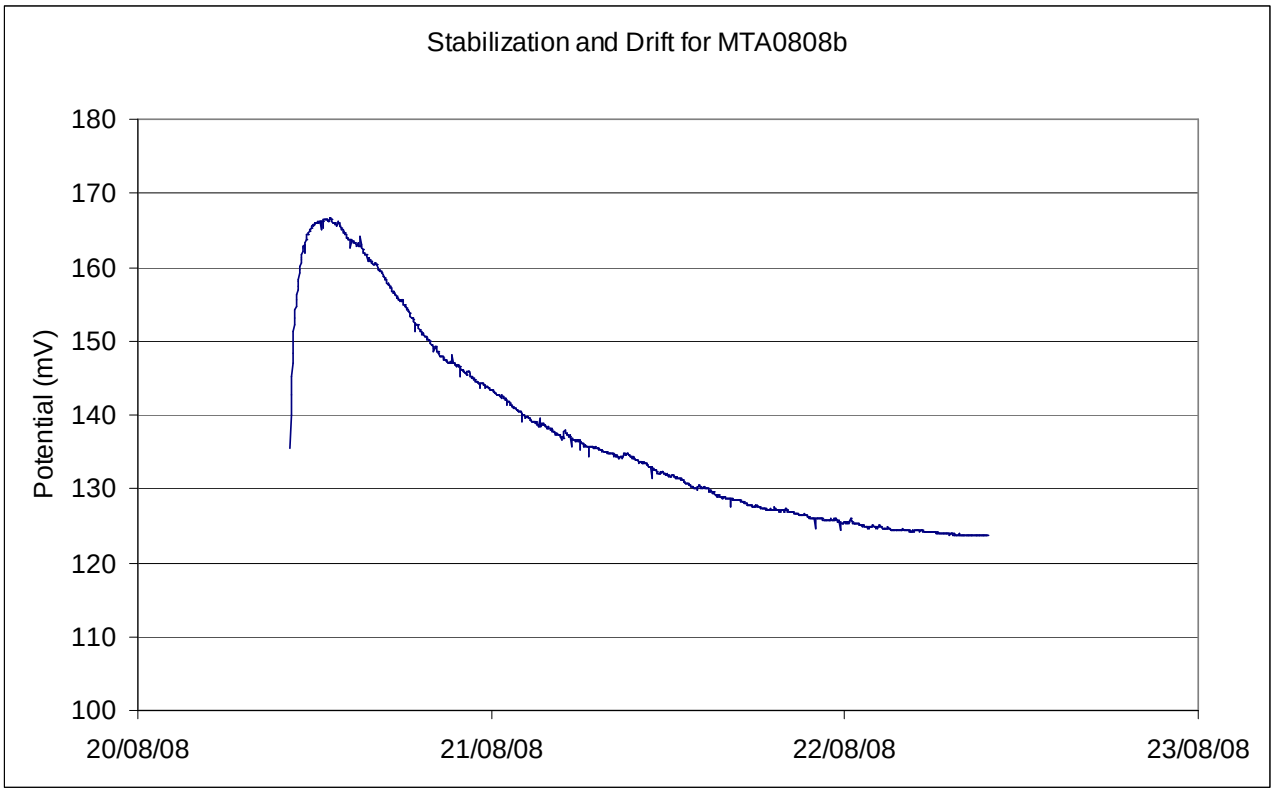

MTA0109a
40
20
0
-20
-40
-60
-80
Potential
0.00001
0.0001
0.001
0.01
0.1
1
Molar Concentration NaCl


MTA0209a
-60
-80
-100
-120
-140
-160
-180
Potential (mV)
0.00001
0.0001
0.001
0.01
0.1
1
Molar Concentration
NaCl
KCl

B2.5 Stabilization data for the MTA sensors where long-term testing was conducted.

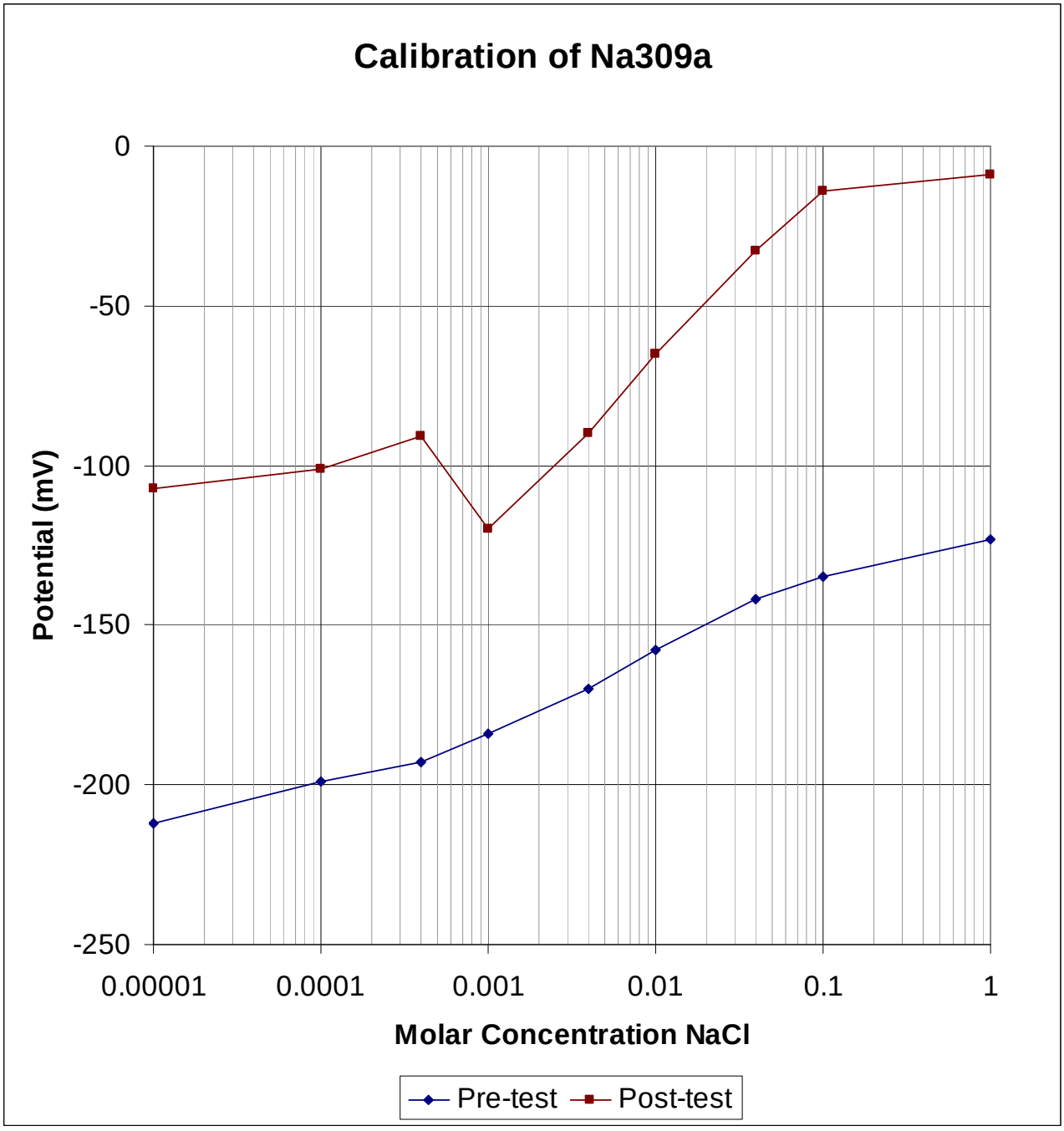




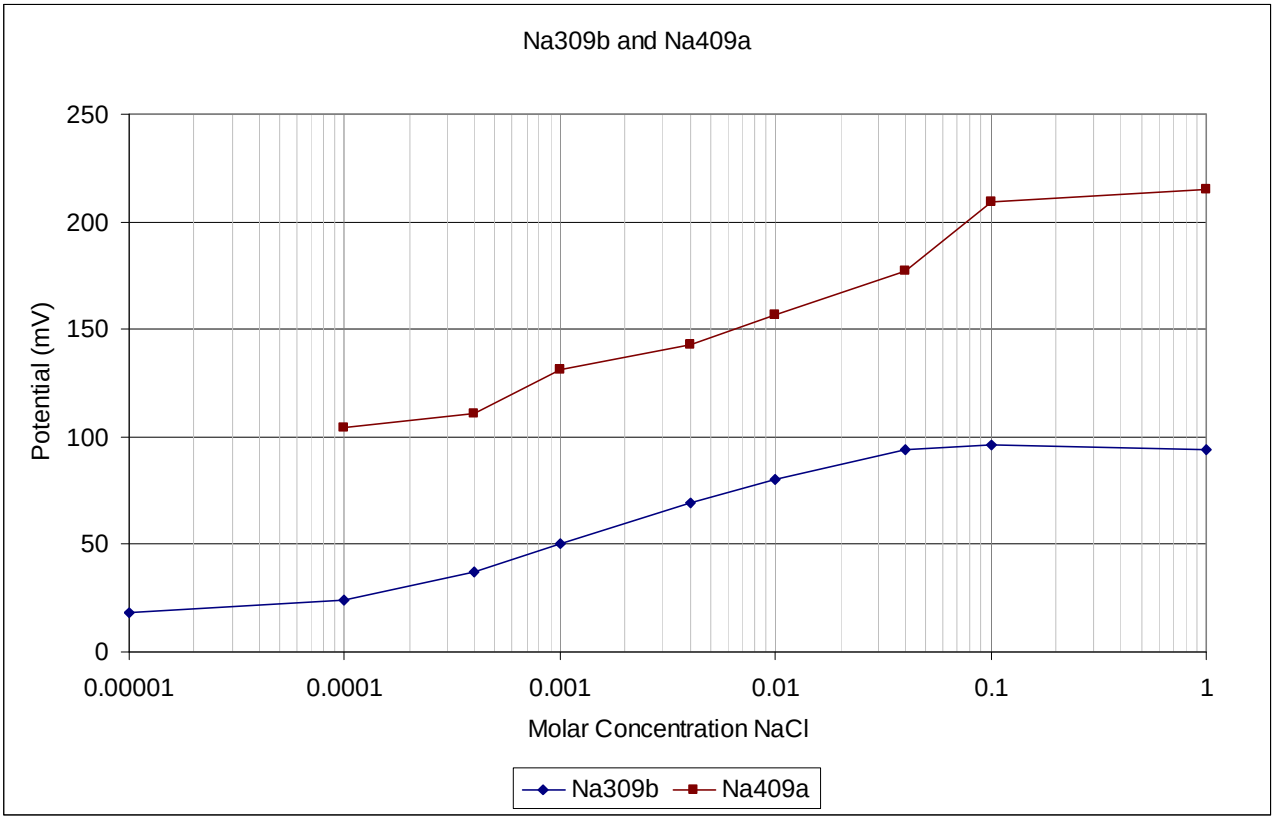

Stabilization and Drift for MTA0808b
Potential (mV)
180
170
160
150
140
130
120
110
100
20/08/08
21/08/08
22/08/08
23/08/08

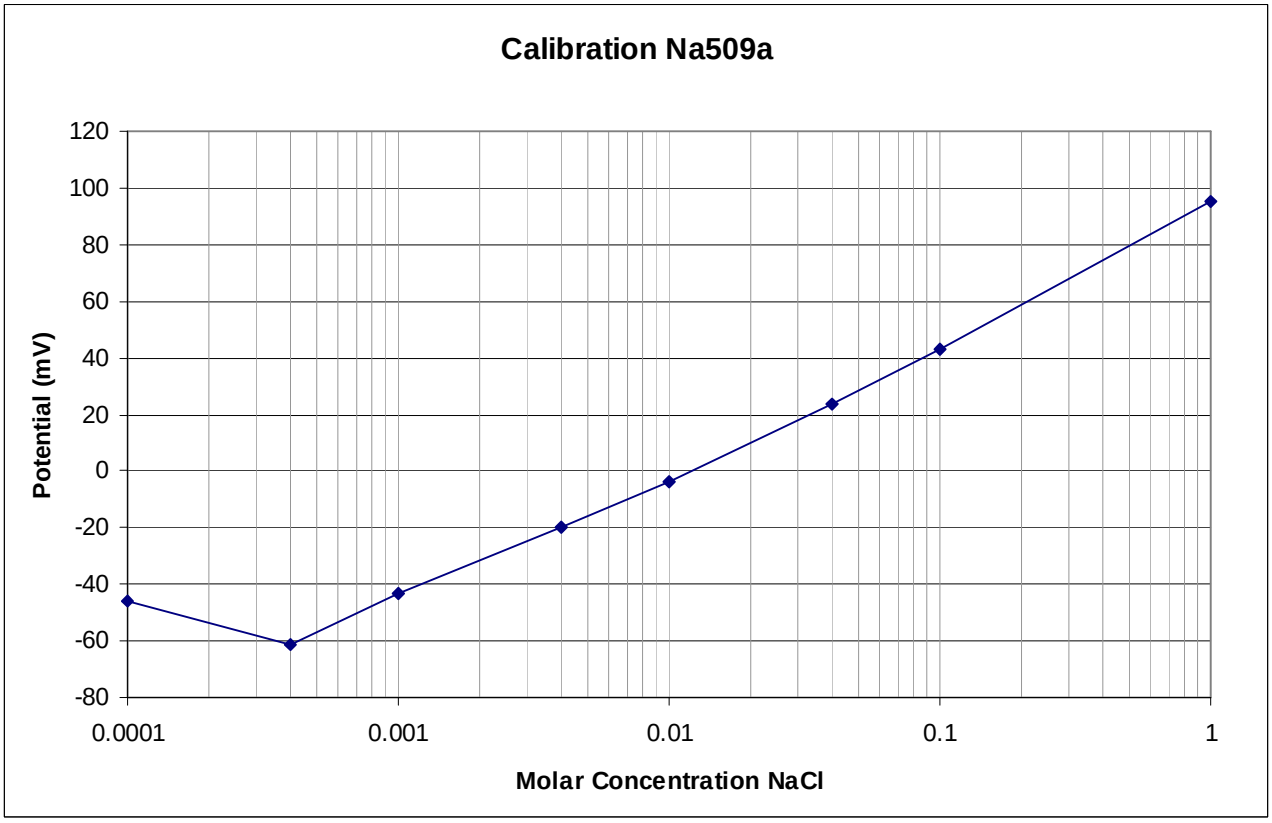
B3. PVC Sensor Series

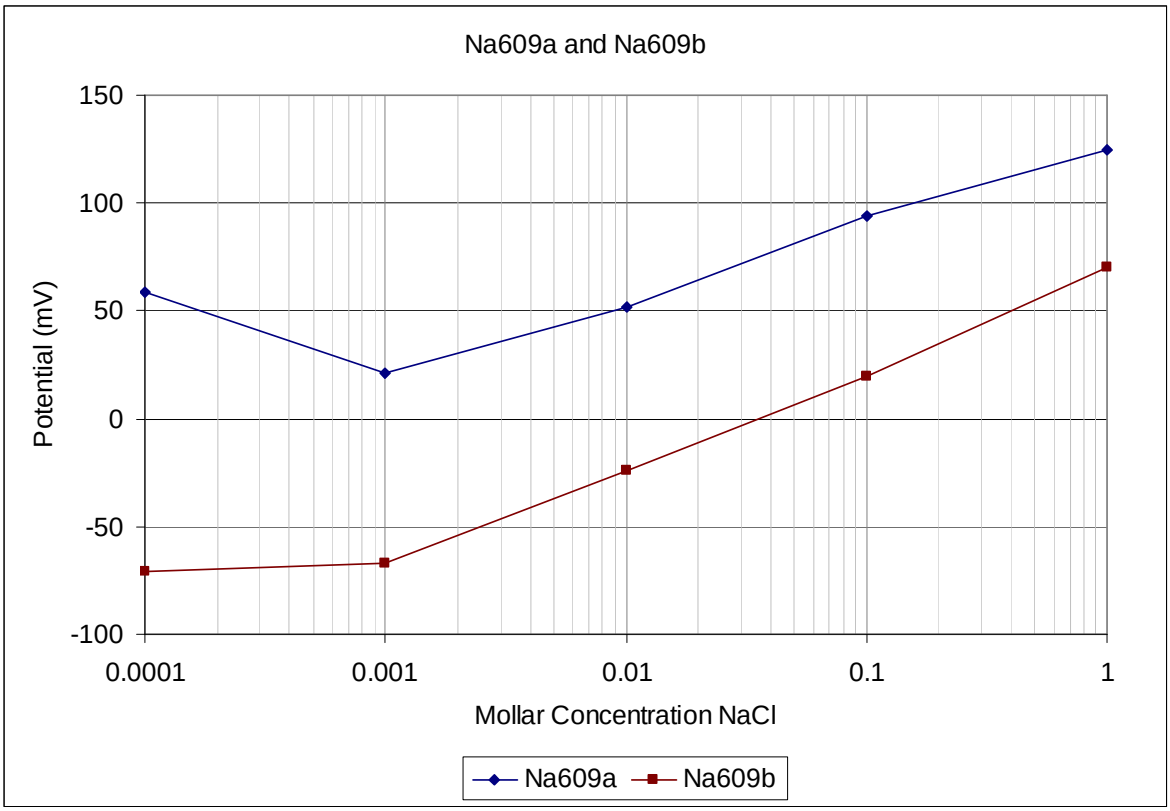
B3.1 Sensor Calibration data for the PVC sensor series, as provided in Table 3, Chapter 4.

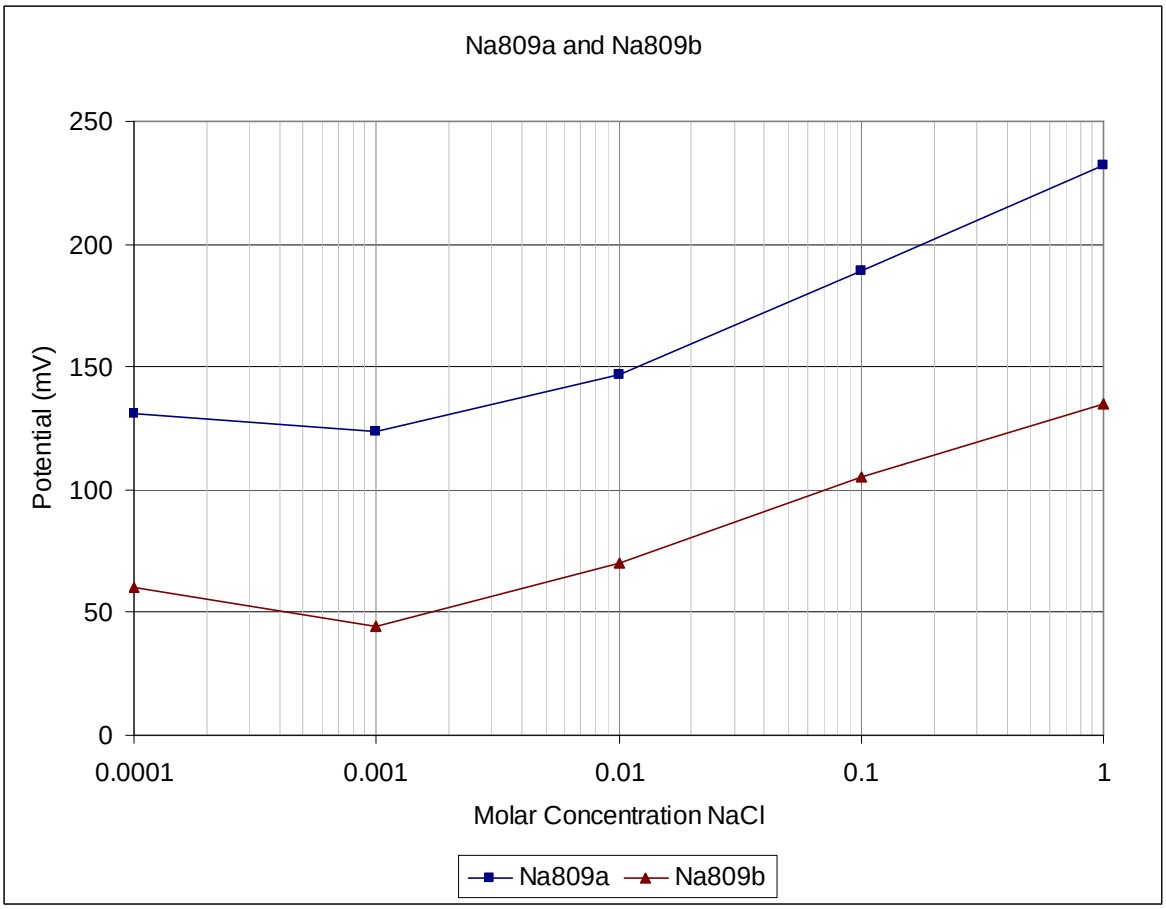


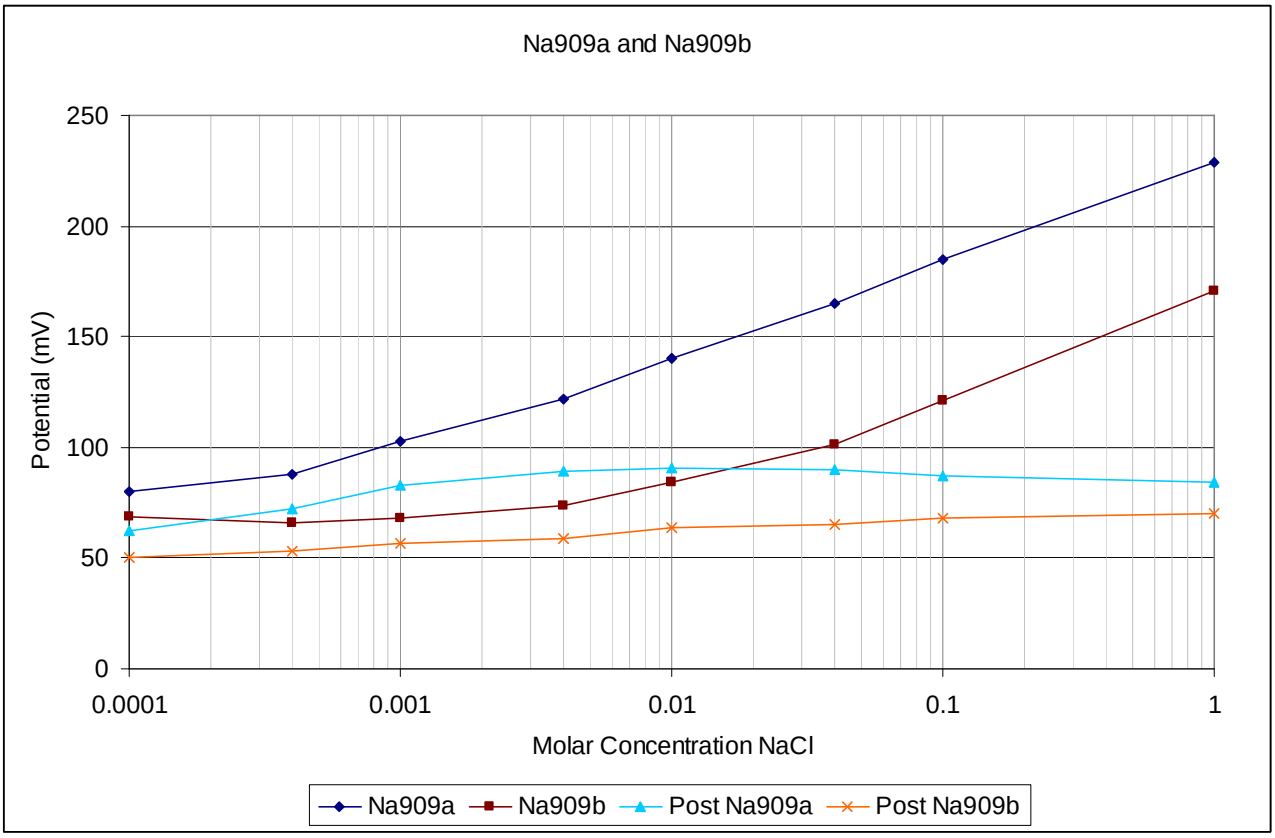
Note: the pre-test and the post-test curves represent the calibration of the sensor before and after (respectively) a four-day laboratory stabilization test. In this case the response of the sensor was better after the four-day test than it was before.

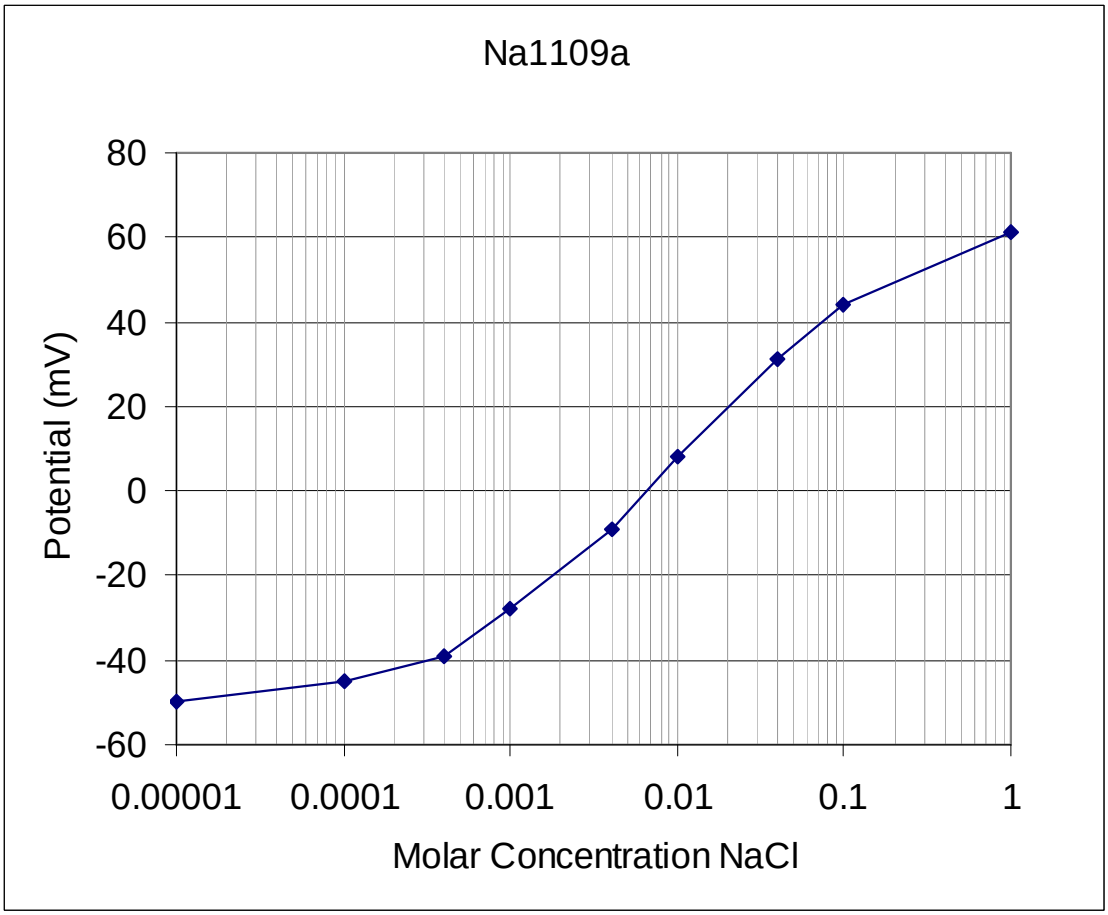

Na309b and Na409a
250
200
150
100
50
0
Potential (mV)
0.00001
0.0001
0.001
0.01
0.1
1
Molar Concentration NaCl
Na309b
Na409a


Calibration Na509a
120
100
80
60
40
20
0
-20
-40
-60
-80
Potential (mV)
0.0001
0.001
0.01
0.1
1
Molar Concentration NaCl

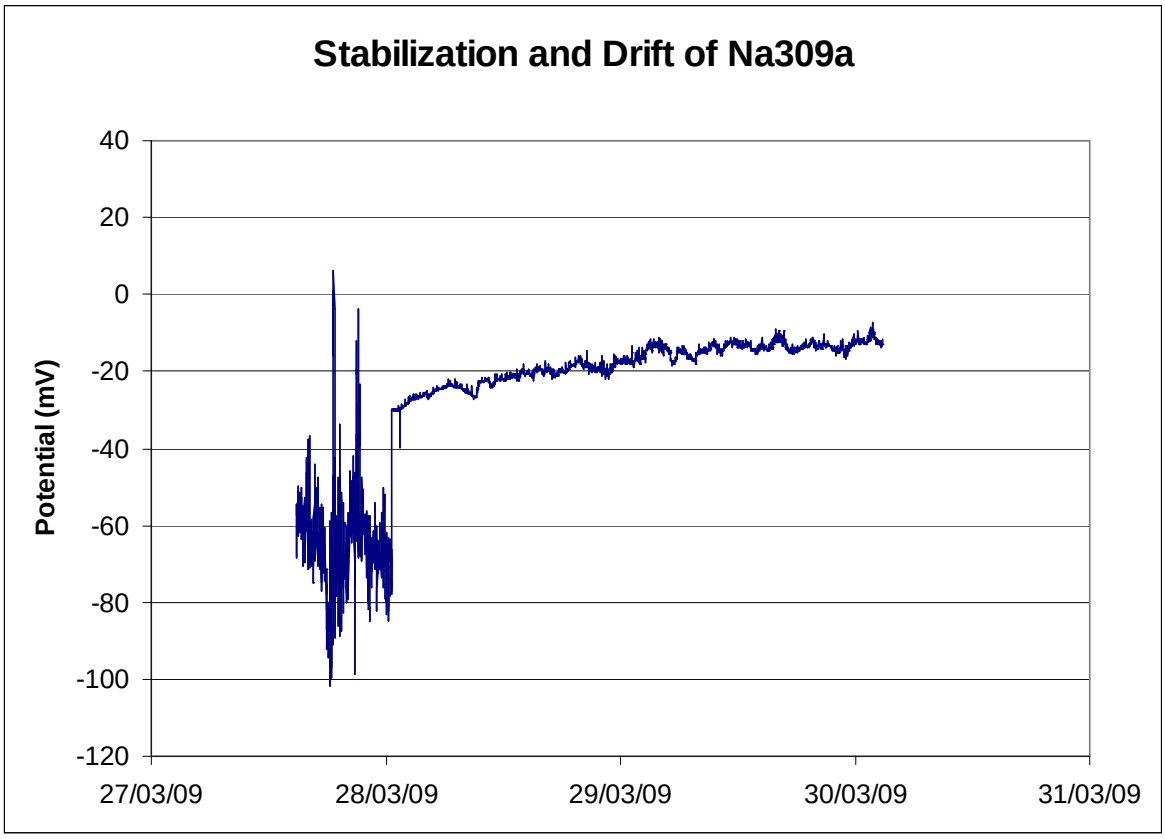

Na609a and Na609b
150
100
50
0
-50
-100
Potential (mV)
0.0001
0.001
0.01
0.1
1
Mollar Concentration NaCl
Na609a
Na609b


Na809a and Na809b
250
200
150
100
50
0
Potential (mV)
0.0001
0.001
0.01
0.1
1
Molar Concentration NaCl
Na809a
Na809b

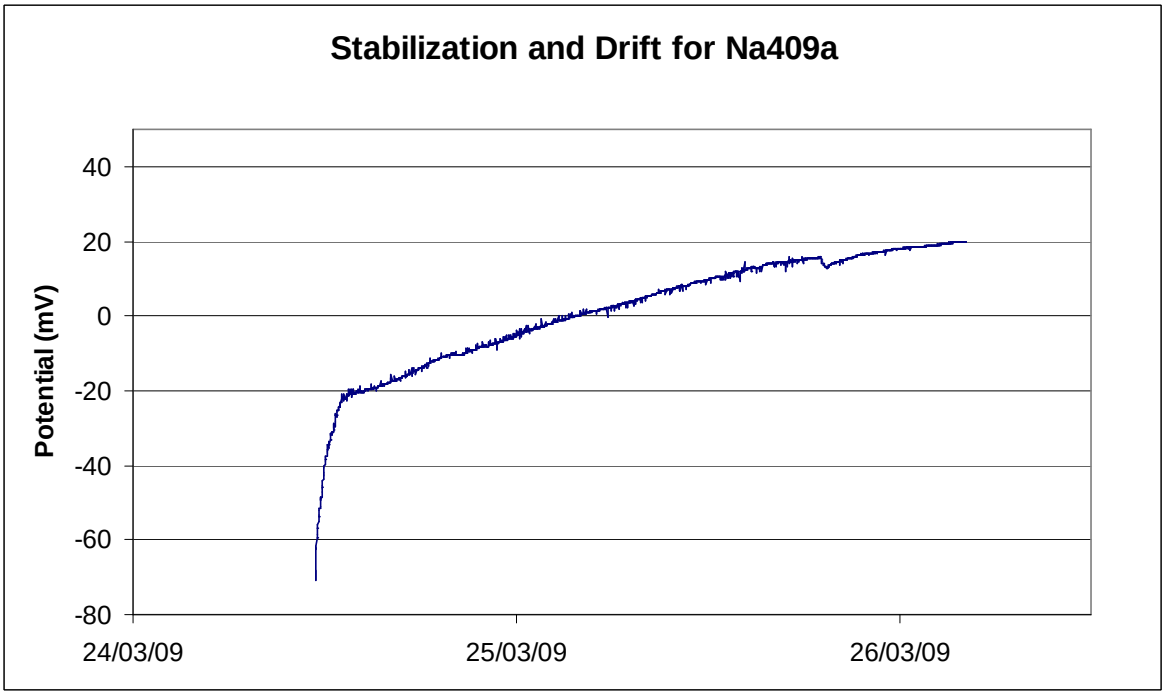

Na909a and Na909b
250
200
150
100
50
0
Potential (mV)
0.0001
0.001
0.01
0.1
1
Molar Concentration NaCl
Na909a
Na909b
Post Na909a
Post Na909b

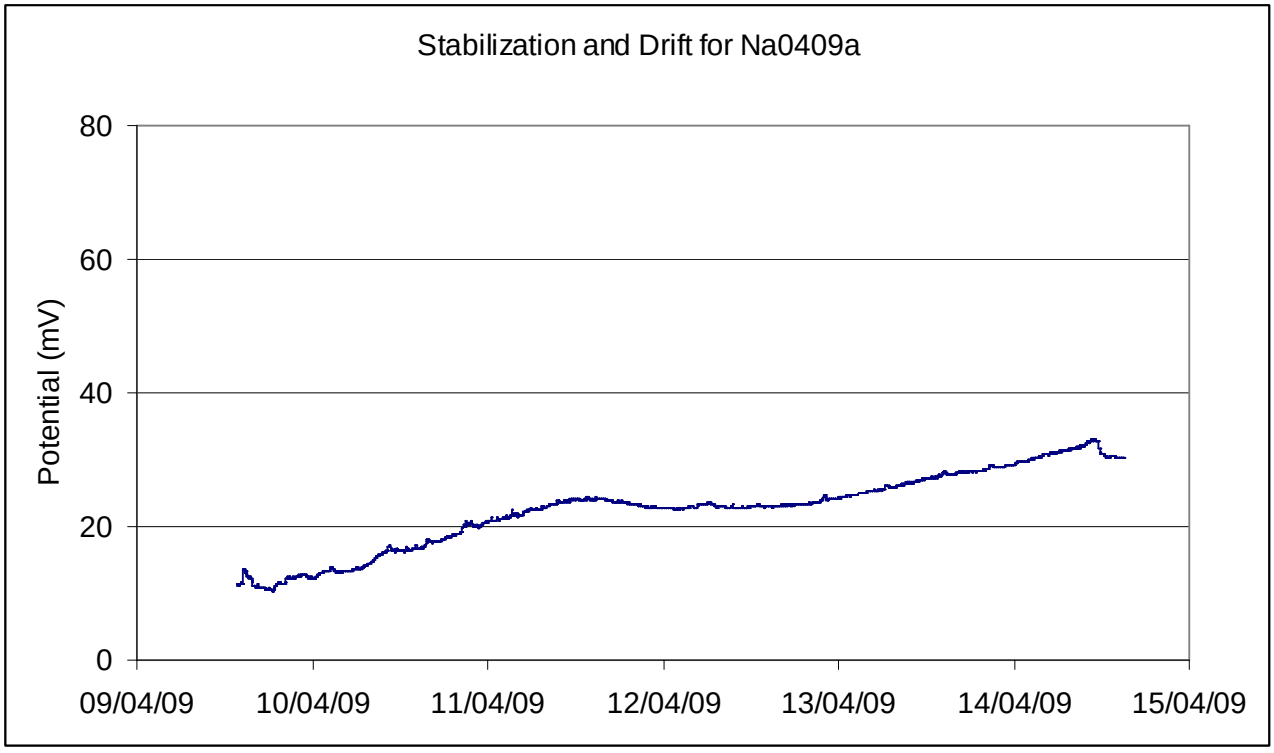

Na1109a
80
60
40
20
0
-20
-40
-60
Potential (mV)
0.00001
0.0001
0.001
0.01
0.1
1
Molar Concentration NaCl

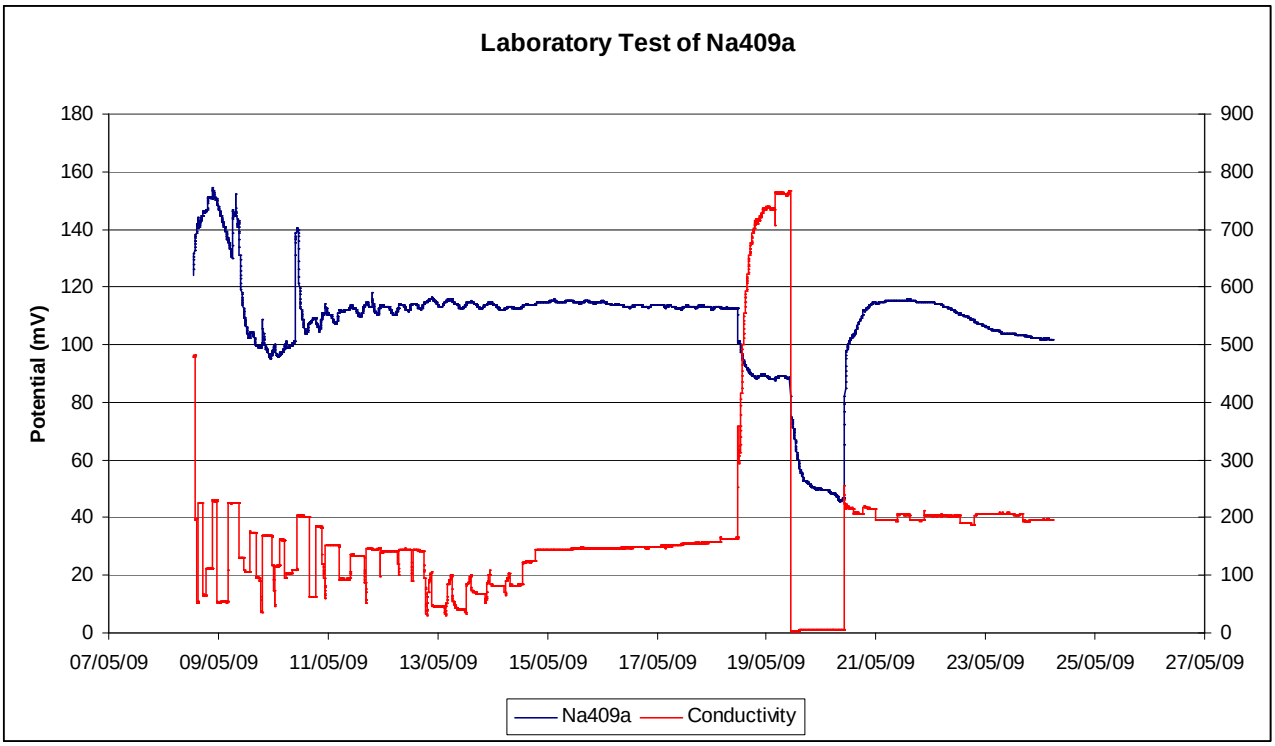
B3.2 Stabilization data for the PVC sensors where long-term testing was conducted.



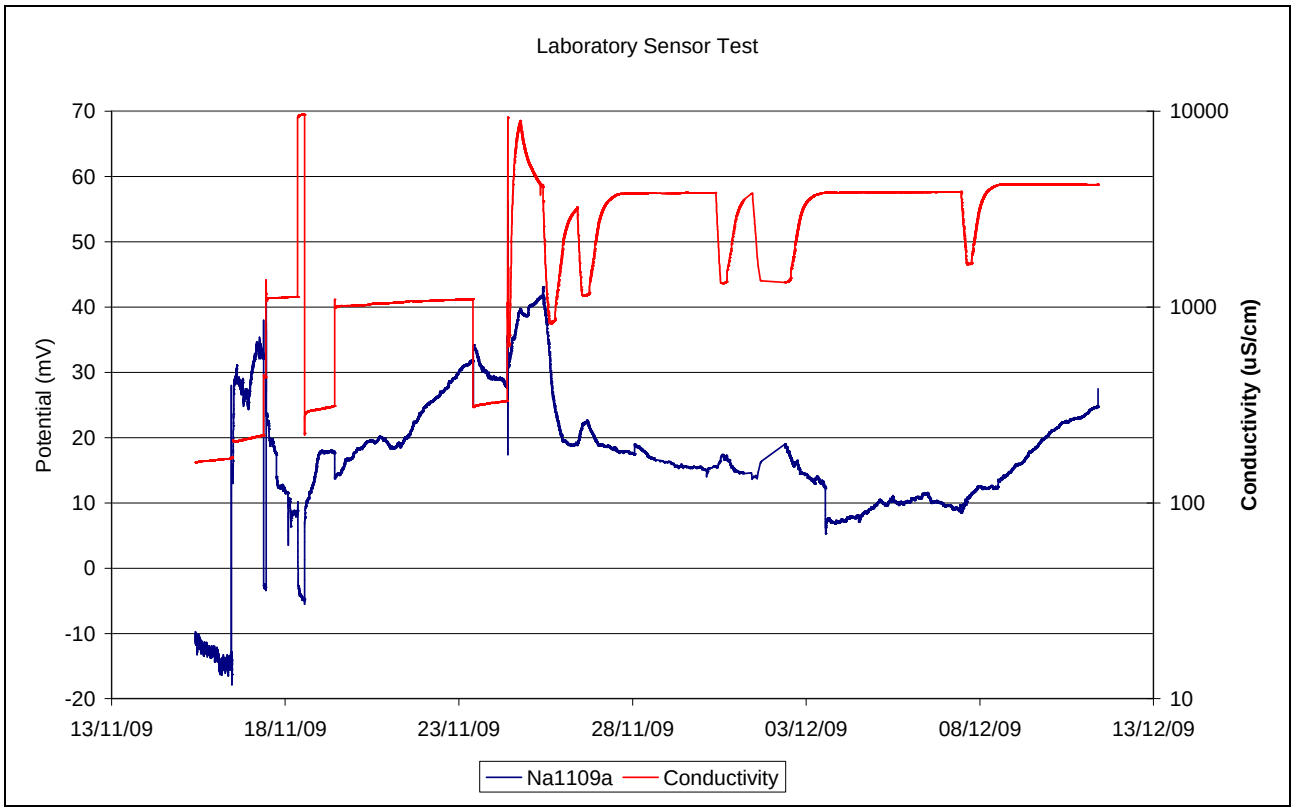
Note: in the test of Na309a, the first day there was a loose contact, creating the unstable response. The contact was fixed, where the signal became stable again.







Note: the test was conducted in changing NaCl concentrations, which are seen in the conductivity response. On the positive change from the 18th of May, 2009, the sensor responded opposite of what it should have, where as on the 19th and 20th, it responded in correctly, just that the size of the response was not in proportion, where it should have been larger on the 19th than the 20th.



Note: the test was conducted in changing NaCl concentrations. The sensor, though very unstable, had a response to the changing concentration as late as November 25, where after it was completely unresponsive to any change.