# Supporting Information for:

# Potentiometric Sensing Array for Monitoring Aquatic Systems

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## SUPPORTING INFORMATION

### *1. Custom-made Instrument GalvaPot v2*

A portable custom-made instrument GalvaPot for decentralized measurements with ionophore based electrodes reported recently[1] was used as the basis for designing new version GalvaPot v2 for field applications. As in GalvaPot, the base for GalvaPot v2 comprises two boards: the acquisition board that contains all the control electronics and the measurement board with all the measurement electronics. For the device to meet the requirements of field application a number of new extension boards were added and the software was updated. A detailed description of the added and modified features is presented in the following section.

### *1.1 Hardware modifications*

The possibility of performing potentiometric measurements has been of key priority. To meet this requirement three vacant analog channels were used that were accessible on the galvanostatic measurement board. This made it possible to create a three channel potentiometric measurement board with a separate common reference. The schematic diagram of the board is shown in Figure S1.

Three inputs and one common reference input are connected to high impedance followers. Optional filters are included on all the signal paths (activable with jumpers). For every single channel the difference between the inputs 1-3 and the common reference is routed to the acquisition bard. As a multichannel potentiometer was needed, a multiplexer made of relays was added to the inputs. Coupling the potentiometer board with the relay boards enabled data acquisition from up to 12 channels. The acquisition speed on the three local channels is about 12 Hz.

Creating relay boards to multiply the number of inputs was performed at the cost of a reduced acquisition speed. Relay boards are organized into three channels (A,B and C) that are able to connect to one of four inputs (1-4) as shown in Figure S2. The relays were inserted into the analog measurement paths. The selection pins are connected to free digital outputs from the acquisition board. Thus by adding the Relay boards three channels have been multiplied by four. When switching the relay, a delay of about 1-s before a new data acquisition had to be introduced. The delay is required for stabilization of oscillating mechanical parts and low-pass filter recovery.

To enable temperature measurements one of the two I2C extension busses accessible in the old design was involved to connect to the new temperature measurement board (see Figure S3). The new board includes an analog-to-digital converter and all the electronics necessary to perform temperature measurements with PT100 sensor.

Galvanic isolation has also been implemented on all power and communication paths. As GalvaPot v2 was designed for performing field measurements in connection with other instruments it was important to eliminate any possible ground loops between the instruments. The power supply is an on-the-shelf isolated DCDC converter at the input. The trigger input has been routed through an optocoupler. Introducing modular interfaces used for communication ports (RS232 to the PC and RS485 to the pumps) made it possible to redesign only these little interfaces instead of modifying the complete design of the Acquisition board. Due to constraints in size and power the communication modules were isolated using magnetic isolator circuits from Analog Devices (circuit reference: ADuM5201).

### *1.2 Software modifications*

The software has been modified to support added hardware features: potentiometric measurements, temperature measurements and relay boards selection; temperature sensor calibration routine has been implemented.

The most complex improvement was the implementation of a protocol enabling the modification of different parameters by the user on field. Two methods were implemented: Experiment Method and Calibration Method. Each method is a list of simple commands with parameters allowing changing the state of pumps, introducing a delay, starting or stopping the measurement.

The procedure starts with Calibration Method running continuously. Upon receipt of external trigger, the GalvaPot v2 stops its Calibration Method, stores the last valid results and starts Experiment Method. When Experiment Method is finished GalvaPot v2 restarts the Calibration Method. The schematic diagram of the whole procedure is presented in Figure S4.

Two method descriptions and measurement results are stored in the local EEPROM memory placed in an I2C bus. The memory size is 64 kB that puts certain limits on the application: the current design allows storage of maximum 50 steps for each of the two methods and 1100 data lines (one data line is composed of time, temperature value and 12 readings corresponding to potentiostatic measurements at 12 channels).

The following limitations must therefore be considered for the reported device: limited number of readings (1100 lines), limited number of method steps (50 per method), limited acquisition speed when the relay is switched (1-s delay) and comparatively complicated and expensive production costs due to a large number of cables.

Hence, the next steps for GalvaPot v2 improvement will be redesigning the acquisition board to add more non-volatile memory (an SD-card, for example) and modifying the measurement boards to enable multichannel design without using the relays.

### *2 ISEs. Preliminary experiments*

Calibration curve for the pH electrode with PVC based membrane doped with tridodecylamine (TDDA) is presented in Figure S6. Calibration was performed in a beaker in stirring conditions. Multiple readings in the range of pH 7 - 9 obtained moving up and down the calibration curve (decreasing pH by adding $H_2SO_4$, increasing pH by adding NaOH) indicate that there is no deviation from linear behaviour in the range required for freshwater analysis.

Calibration curves for ammonium electrodes with PVC based TDDA doped membranes of different composition are shown in Figure S8. Properties of PVC based membrane doped with TDDA were studied thoroughly in the past.[2, 3] To the best of our knowledge, no considerable improvements of ammonium ISEs has been made in the two recent decades. Detection limits of the membranes developed do not go below the order $10^{-6}$ M. Membranes of few different compositions were investigated here to choose the one possessing the lowest detection limit. As observed, membrane containing no additional ion exchanger (M2) exhibits lowest detection limit both at pH 8 (Figure S8a) and with 0.1 mM KCl background (Figure S8b). Thus the membrane containing no additional ion exchanger was chosen for field experiments. It can be seen though that 0.1 mM potassium background (close to the range of potassium concentration in fresh waters) deteriorates the lower limit of detection (LDL) of ammonium ISE by approximately one logarithmic unit therefore $a_{\mathrm{LDL}}$ being around 10 $\mu$M with the indicated background.

### *3 Calculation of single ion activity in calibration solutions*

Single ion activities $a_i$ in calibration solutions were calculated based on concentration values indicated in Table 1 (main text) according to the conventional relationship:

$$a_i = \gamma_i \cdot c_i \tag{S1}$$

where $\gamma_i$ is single ion activity coefficient and $c_i$ the molar concentration of ion *i*.

$\gamma_i$ was calculated in three steps:

1. The ionic strength $I$ of the calibration solution was calculated using the following equation:

$$I = 0.5 \sum_i z_i^2 c_i \tag{S2}$$

2. Mean ion activity coefficients $\gamma_\pm$ for carbonate, ammonium and nitrate salts in mixed calibration solutions were calculated using the first approximation of the Debye-Hückel theory:

$$\log \gamma_\pm = -A \left| z_+ z_- \right| \sqrt{I} \tag{S3}$$

Mean ion activity coefficients $\gamma_{\pm}$ for concentrated calcium chloride solutions (1 mM and 10 mM $CaCl_2$) were calculated using the extended Debye-Hückel theory:

$$\log \gamma_{\pm} = -\frac{A|z_{+}z_{-}|\sqrt{I}}{1+B\sqrt{I}} + CI \tag{S4}$$

$z_{+}$ and $z_{-}$ in equations S2 and S3 are charges of the ion $i$ and corresponding counter ion; monovalent counter ions were considered since major ion species (sodium, bicarbonate, chloride) in calibration solutions are monovalent, and $A$ is a parameter that is a function of temperature ($A$ = 0.5108 at 25$^{O}$C). $A$ is proportional to $T^{-3/2}$ (T is temperature in Kelvin) and changes inconsiderably in the range of the explored temperatures, thus for $\gamma_i$ estimation we assume $A$ to be constant. $B$ and $C$ are fittable parameters ($B \sim T^{-1/2}$, $C$ with an unknown dependence on temperature) that are tabulated for most electrolytes.[4]

3. The simplified Debye-Hückel convention was used to calculate single ion activity coefficients $\gamma_i$ ($\gamma_{Ca^{2+}}$, $\gamma_{NH_4^+}$, $\gamma_{NO_3^-}$ and $\gamma_{CO_3^{2-}}$) considering monovalent counter ions, as mentioned earlier:

$$\begin{aligned} \log \gamma_{+} &= \left|\frac{z_{+}}{z_{-}}\right| \log \gamma_{\pm} \quad (a) \\ \log \gamma_{-} &= \left|\frac{z_{-}}{z_{+}}\right| \log \gamma_{\pm} \quad (b) \end{aligned} \tag{S5}$$

The calculation procedure may be illustrated using carbonate activity coefficient calculation as an example. First, the ionic strength of the calibration solutions was calculated with equation S2 considering concentrations and charges of all the species present: $K^+$, $Na^+$ (including sodium added in the form of NaOH for adjusting the pH of calibration solution 1, $NH_4^+$, $Ca^{2+}$ (free), $[Ca(NTA)]^-$, $Cl^-$, $HCO_3^-$, $CO_3^{2-}$, $NO_3^-$, $[OCH_2(HOCH_2)_2CNH_2]^-$ (dissociated TRIS), $[N(CH_2CO_2)_3]^{3-}$, $[NCH_2CO_2H(CH_2CO_2)_2]^{2-}$ (from NTA dissociation), $SO_4^{2-}$ (for calibration solution 2 acidified with $H_2SO_4$). An ionic strength of 10.5 mM and

11.2 mM was obtained for calibration solutions 1 and 2, respectively. Second, mean ion activity coefficients $\gamma_{\pm}(Na_2CO_3)$ were calculated using equation S3 where $z_+ = 1$, $z_- = -2$, $A = 0.5108$ resulting in $\log\gamma_{\pm}(Na_2CO_3)$ being -0.105 and -0.108 respectively. Finally, single ion activity coefficients $\gamma_{CO_3^{2-}}$ were calculated according to equation S5b where $z_+ = 1$, $z_- = -2$ giving $\gamma_{CO_3^{2-}} = 0.62$ for calibration solution 1 and $\gamma_{CO_3^{2-}} = 0.61$ for calibration solution 2.

To calculate single ion activities $a_i$ according to equation S1, the pH measured by commercial glass electrode was used to correct carbonate and ammonium concentrations $c_i$ for speciation using the acid dissociation constants $(K_{a2}(H_2CO_3) = \frac{c_{H+} \cdot c_{CO_3^{2-}}}{c_{HCO_3^-}}, pK_{a2} = 10.32;\ K_a(NH_4^+) = \frac{c_{H+} \cdot c_{NH_3}}{c_{NH_4^+}}, pK_{a2} = 9.25)$.

Table S1

**a. Experiment Method**

| Step N | Command | Command description |
|---|---|---|
| 1 | Pump 0003 0001 0202 0000 | Start Pump 3 counterclockwise with speed 20.2 rpm |
| 2 | Pump 0002 0000 0202 0000 | Stop Pump 2 |
| 3 | Pump 0001 0000 0202 0000 | Stop Pump 1 |
| 4 | Pump 0004 0001 0024 0000 | Start Pump 4 counterclockwise with speed 2.4 rpm |
| 5 | Pump 0005 0001 0024 0000 | Start Pump 5 counterclockwise with speed 2.4 rpm |
| 6 | Pump 0006 0001 0202 0001 | Start Pump 6 counterclockwise with speed 20.2 rpm |
| 7 | Dely 0180 | Delay 180 sec |
| 8 | MesP 0008 0006 | Measuring potential on eight channels averaging over 6 seconds for one channel |
| 9 | MesP 0008 0006 | Measuring potential on eight channels averaging over 6 seconds for one channel |
| 10 | MesP 0008 0006 | Measuring potential on eight channels averaging over 6 seconds for one channel |
| 11 | MesP 0008 0006 | Measuring potential on eight channels averaging over 6 seconds for one channel |
| 12 | MesP 0008 0006 | Measuring potential on eight channels averaging over 6 seconds for one channel |
| 13 | Pump 0001 0001 0202 0000 | Start Pump 1 counterclockwise with speed 20.2 rpm |
| 14 | Pump 0003 0000 0202 0000 | Stop Pump 3 |
| 15 | Pump 0002 0000 0202 0000 | Stop Pump 2 |
| 16 | Pump 0004 0001 0024 0000 | Start Pump 4 counterclockwise with speed 2.4 rpm |
| 17 | Pump 0005 0001 0024 0000 | Start Pump 5 counterclockwise with speed 2.4 rpm |
| 18 | Pump 0006 0001 0202 0001 | Start Pump 6 counterclockwise with speed 20.2 rpm |
| 19 | MesP 0008 0006 | Measuring potential on eight channels averaging over 6 seconds for one channel |
| 20 | MesP 0008 0006 | Measuring potential on eight channels averaging over 6 seconds for one channel |
| 21 | MesP 0008 0006 | Measuring potential on eight channels averaging over 6 seconds for one channel |
| 22 | End | End of Experiment Method |

**b. Calibration Method**

| Step N | Command | Command description |
|---|---|---|
| 1 | Pump 0001 0001 0202 0000 | Start Pump 1 counterclockwise with speed 20.2 rpm |
| 2 | Pump 0002 0000 0202 0000 | Stop Pump 2 |
| 3 | Pump 0003 0000 0202 0000 | Stop Pump 3 |
| 4 | Pump 0004 0001 0024 0000 | Start Pump 4 counterclockwise with speed 2.4 rpm |
| 5 | Pump 0005 0001 0024 0000 | Start Pump 5 counterclockwise with speed 2.4 rpm |
| 6 | Pump 0006 0001 0202 0001 | Start Pump 6 counterclockwise with speed 20.2 rpm |
| 7 | MesP 0008 0006 | Measuring potential on eight channels averaging over 6 seconds for one channel |
| 8 | MesP 0008 0006 | Measuring potential on eight channels averaging over 6 seconds for one channel |

| | | |
|---|---|---|
| 9 | MesP 0008 0006 | Measuring potential on eight channels averaging over 6 seconds for one channel |
| 10 | MesP 0008 0006 | Measuring potential on eight channels averaging over 6 seconds for one channel |
| 11 | MesP 0008 0006 | Measuring potential on eight channels averaging over 6 seconds for one channel |
| 12 | MesP 0008 0006 | Measuring potential on eight channels averaging over 6 seconds for one channel |
| 13 | MesP 0008 0006 | Measuring potential on eight channels averaging over 6 seconds for one channel |
| 14 | MesP 0008 0006 | Measuring potential on eight channels averaging over 6 seconds for one channel |
| 15 | Pump 0002 0001 0202 0000 | Start Pump 2 counterclockwise with speed 20.2 rpm |
| 16 | Pump 0001 0000 0202 0000 | Stop Pump 1 |
| 17 | Pump 0003 0000 0202 0000 | Stop Pump 3 |
| 18 | Pump 0004 0001 0024 0000 | Start Pump 4 counterclockwise with speed 2.4 rpm |
| 19 | Pump 0005 0001 0024 0000 | Start Pump 5 counterclockwise with speed 2.4 rpm |
| 20 | Pump 0006 0001 0202 0001 | Start Pump 6 counterclockwise with speed 20.2 rpm |
| 21 | MesP 0008 0006 | Measuring potential on eight channels averaging over 6 seconds for one channel |
| 22 | Dely 0240 | Delay 240 sec |
| 23 | MesP 0008 0006 | Measuring potential on eight channels averaging over 6 seconds for one channel |
| 24 | MesP 0008 0006 | Measuring potential on eight channels averaging over 6 seconds for one channel |
| 25 | MesP 0008 0006 | Measuring potential on eight channels averaging over 6 seconds for one channel |
| 26 | Pump 0001 0001 0202 0000 | Start Pump 1 counterclockwise with speed 20.2 rpm |
| 27 | Pump 0002 0000 0202 0000 | Stop Pump 2 |
| 28 | Pump 0003 0000 0202 0000 | Stop Pump 3 |
| 29 | Pump 0004 0001 0024 0000 | Start Pump 4 counterclockwise with speed 2.4 rpm |
| 30 | Pump 0005 0001 0024 0000 | Start Pump 5 counterclockwise with speed 2.4 rpm |
| 31 | Pump 0006 0001 0202 0001 | Start Pump 6 counterclockwise with speed 20.2 rpm |
| 32 | MesP 0008 0006 | Measuring potential on eight channels averaging over 6 seconds for one channel |
| 33 | MesP 0008 0006 | Measuring potential on eight channels averaging over 6 seconds for one channel |
| 34 | MesP 0008 0006 | Measuring potential on eight channels averaging over 6 seconds for one channel |
| 35 | MesP 0008 0006 | Measuring potential on eight channels averaging over 6 seconds for one channel |
| 36 | End | End of Calibration Method |

| | |
|---|---|
| Table S1 | GalvaPot method description as exemplified by the method chosen for the experiment performed on 21-22.08.2014: (a) Experiment Method and (b) Calibration Method. |
| Figure S1 | Schematic diagram of Potentiometric measurement board in GalvaPot v2. |
| Figure S2 | Schematic diagram of Relay board in GalvaPot v2. |
| Figure S3 | Schematic diagram of Temperature measurement board in GalvaPot v2. |
| Figure S4 | Working modes of GalvaPot v2. |
| Figure S5 | Schematic diagram of automated potentiometric detection arrangement reported. |
| Figure S6 | Calibration curve for the pH electrode with PVC based membrane doped with tridodecylamine (TDDA). Calibration was performed in a beaker in stirring conditions. |
| Figure S7 | Calibration curve for nitrate ISE obtained using flow cell presented in Figure 1. Flow rate 0.28 mL/min, background solution composition (in total concentrations): TRIS 10 mM, NTA 3 mM, KCl 130 $\mu$M, $CaCl_2 \cdot 2H_2O$ 1 mM, $NaHCO_3$ 5 mM at pH 7.8. |
| Figure S8 | Calibration curves for ammonium electrodes with PVC based membranes of the following composition: (M1) nonactin 40 mmol/kg, KTpClPB 10 mmol/kg, PVC 64 mg, o-NPOE 127 mg; (M2) nonactin 3 mmol/kg, PVC 64 mg, o-NPOE 141 mg, no additional ion exchanger; (M3) nonactin 14 mmol/kg, KTpClPB 3.5 mmol/kg, PVC 67 mg, o-NPOE 130 mg; (M4) nonactin 20 mmol/kg, KTpClPB 7 mmol/kg, PVC 65 mg, o-NPOE 132 mg. Calibration was performed in a beaker in stirring conditions (a) at pH 8; (b) in background solution containing 100 $\mu$M KCl (pH ca. 6). |
| Figure S9 | Bracket calibrations for ISEs integrated into field monitoring: (a) calcium PVC based electrode; (b) ammonium PVC based electrode; (c) carbonate and nitrate PVC based electrodes; (d) pH PVC based and commercial glass electrodes. Calibrations were obtained in the field in flow conditions before starting field monitoring. |

Figure S10 Stability of calibration during 90 hours of field measurements for nitrate (a,A), carbonate (b,B), pH (c,C) and calcium (d,D) ISEs. (a,b,c,d) EMF values (mV) for calibration solutions 1 (circles) and 2 (diamonds). (A,B,C,D) EMF difference (mV) between calibration solution 2 and calibration solution 1. The vertical dotted lines indicate the time when the calibration solution bottle was replaced with a new portion of calibration solution having slightly different pH.

## REFERENCES

1. S. Jeanneret, G. A. Crespo, M. Ghahraman Afshar and E. Bakker, *Sensors and Actuators B*, 2015, **207**, 631-639.
2. M. S. Ghauri and J. D. Thomas, *Analyst*, 1994, **119**, 2323-2326.
3. O. G. Davies, G. J. Moody and J. D. R. Thomas, *Analyst*, 1988, **113**, 497-500.
4. P. C. Meier, *Anal. Chim. Acta*, 1982, **136**, 363-368.

Figure S1

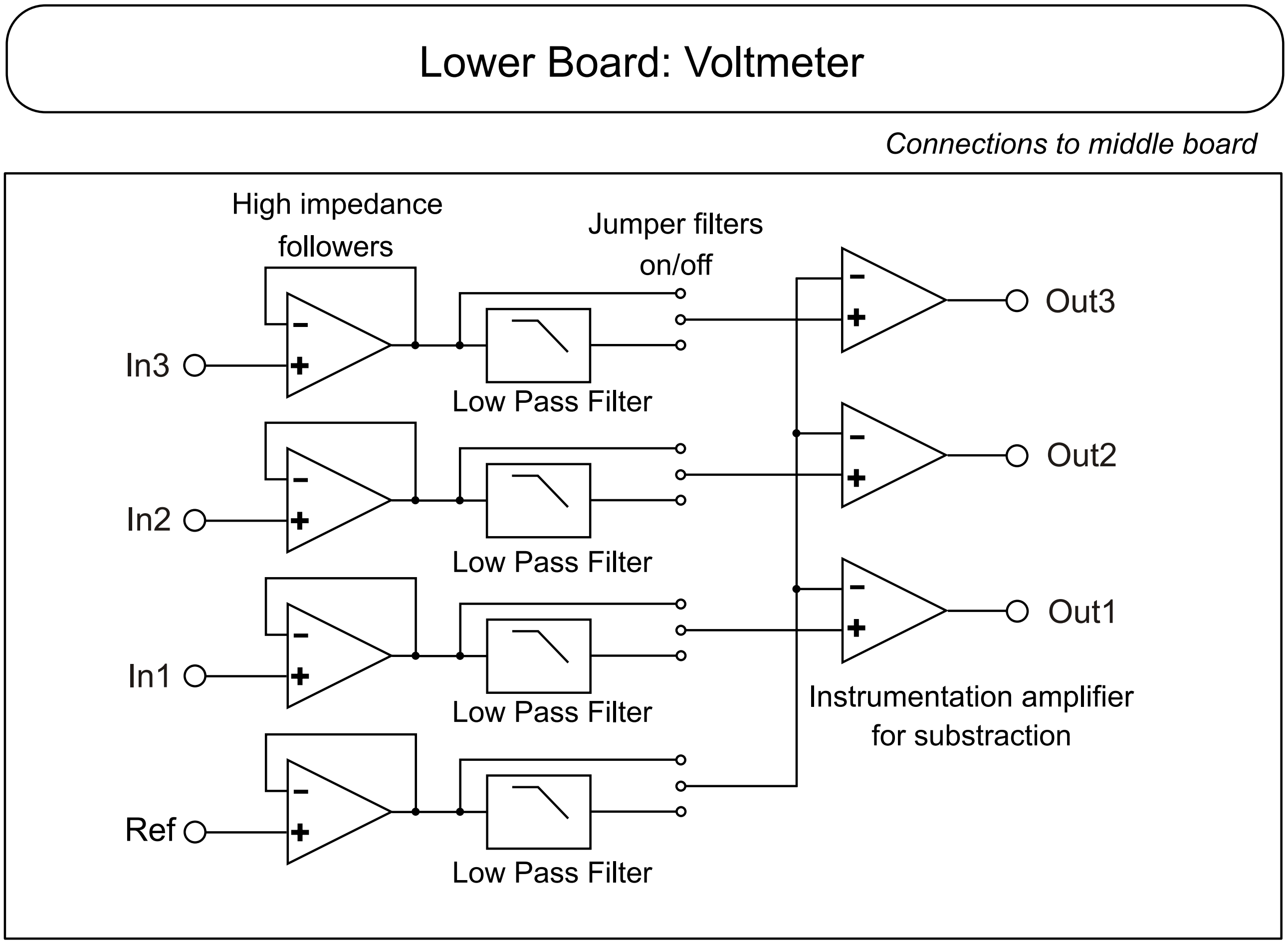

Lower Board: Voltmeter
Connections to middle board
High impedance followers
Jumper filters on/off
In3
In2
In1
Ref
Low Pass Filter
Low Pass Filter
Low Pass Filter
Low Pass Filter
Out3
Out2
Out1
Instrumentation amplifier for substraction

Figure S2

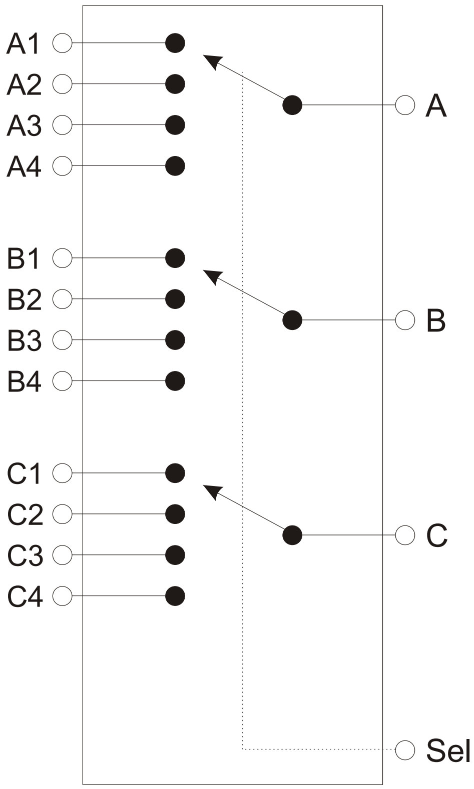


Figure S3

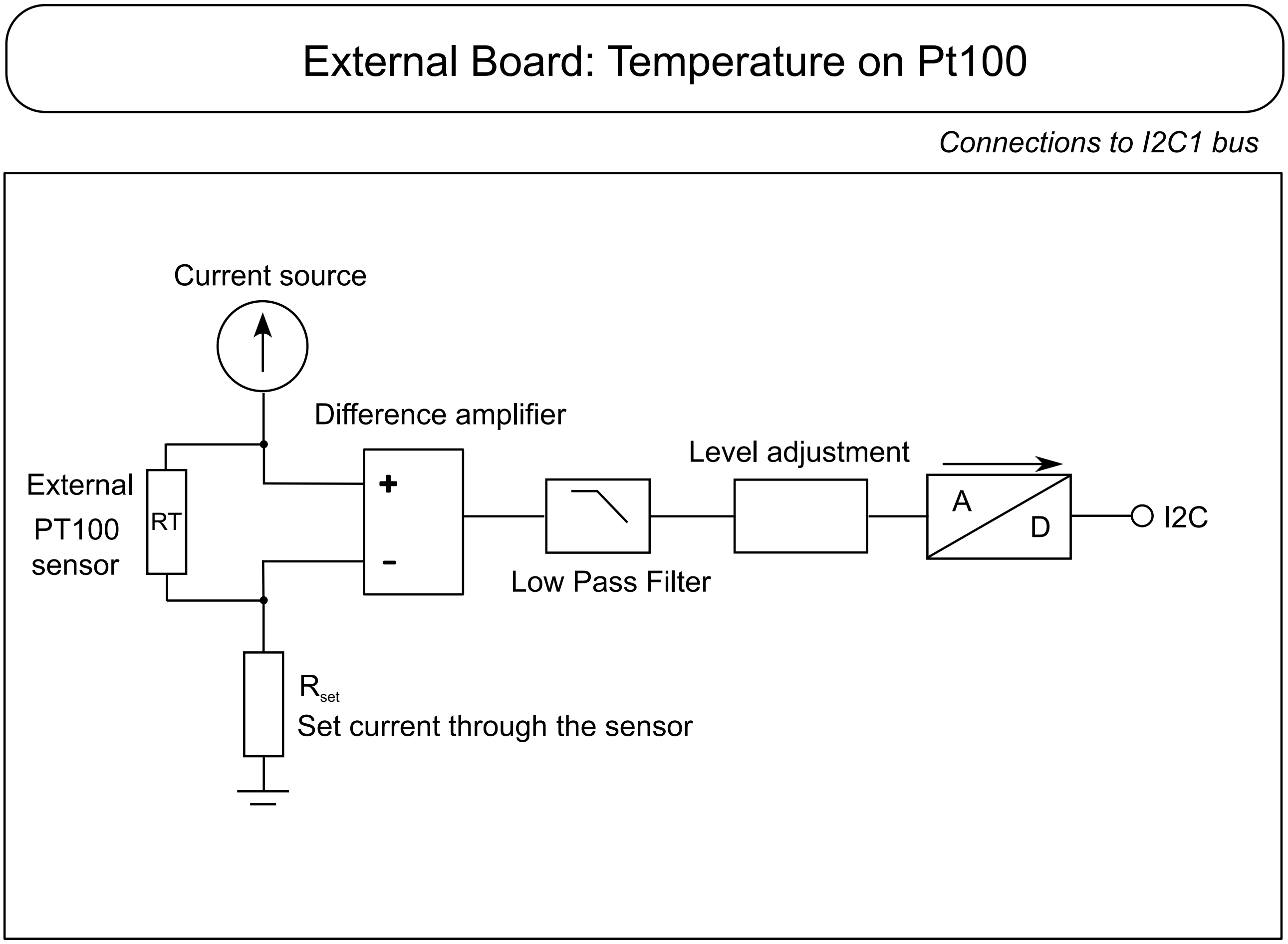
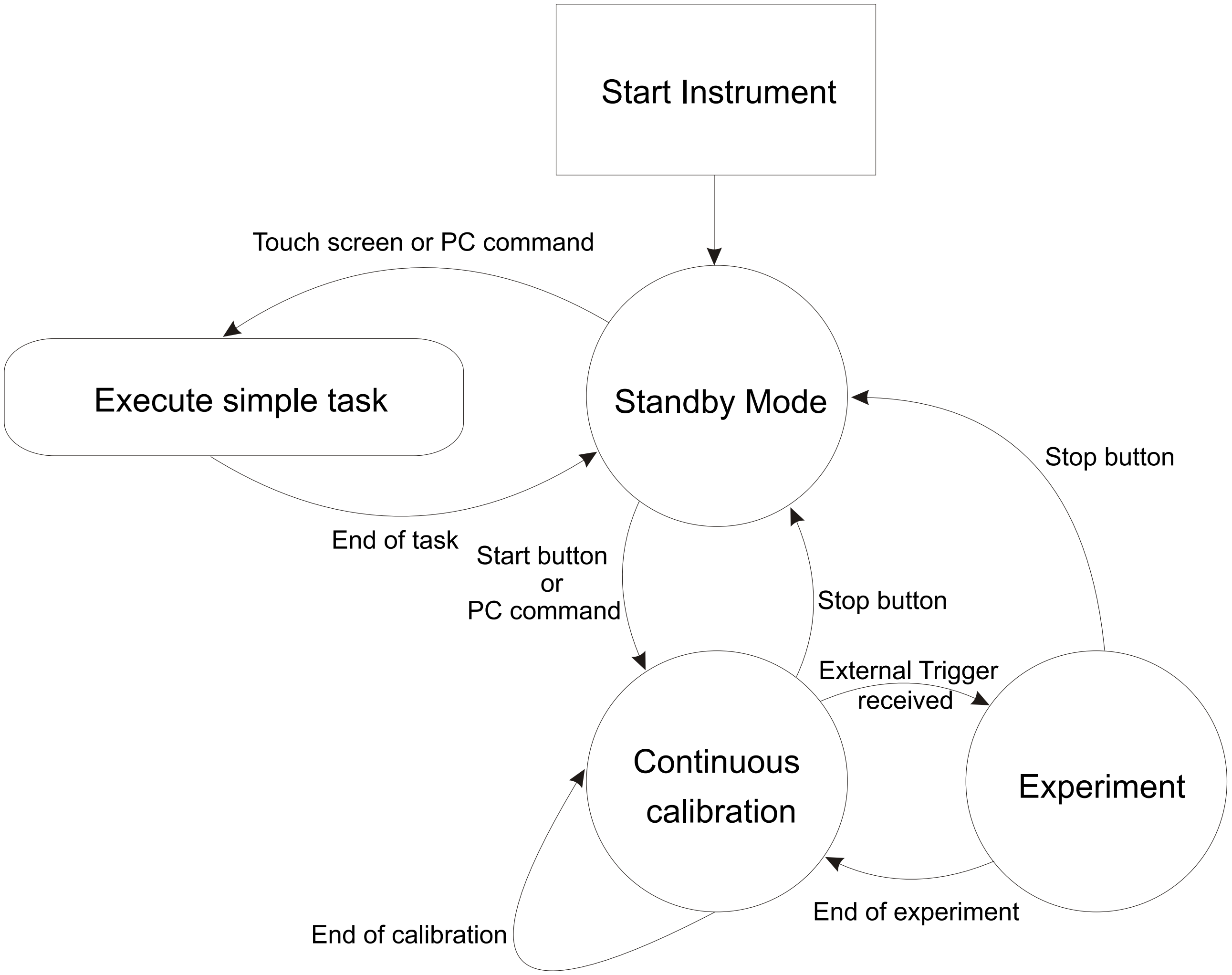

External Board: Temperature on Pt100
Connections to I2C1 bus
Current source
Difference amplifier
+
-
Level adjustment
External
PT100
sensor
RT
A
D
I2C
Low Pass Filter
$R_{set}$
Set current through the sensor

Figure S4



Start Instrument
Touch screen or PC command
Execute simple task
Standby Mode
Stop button
End of task
Start button or PC command
Stop button
External Trigger received
Continuous calibration
Experiment
End of calibration
End of experiment

Figure S5

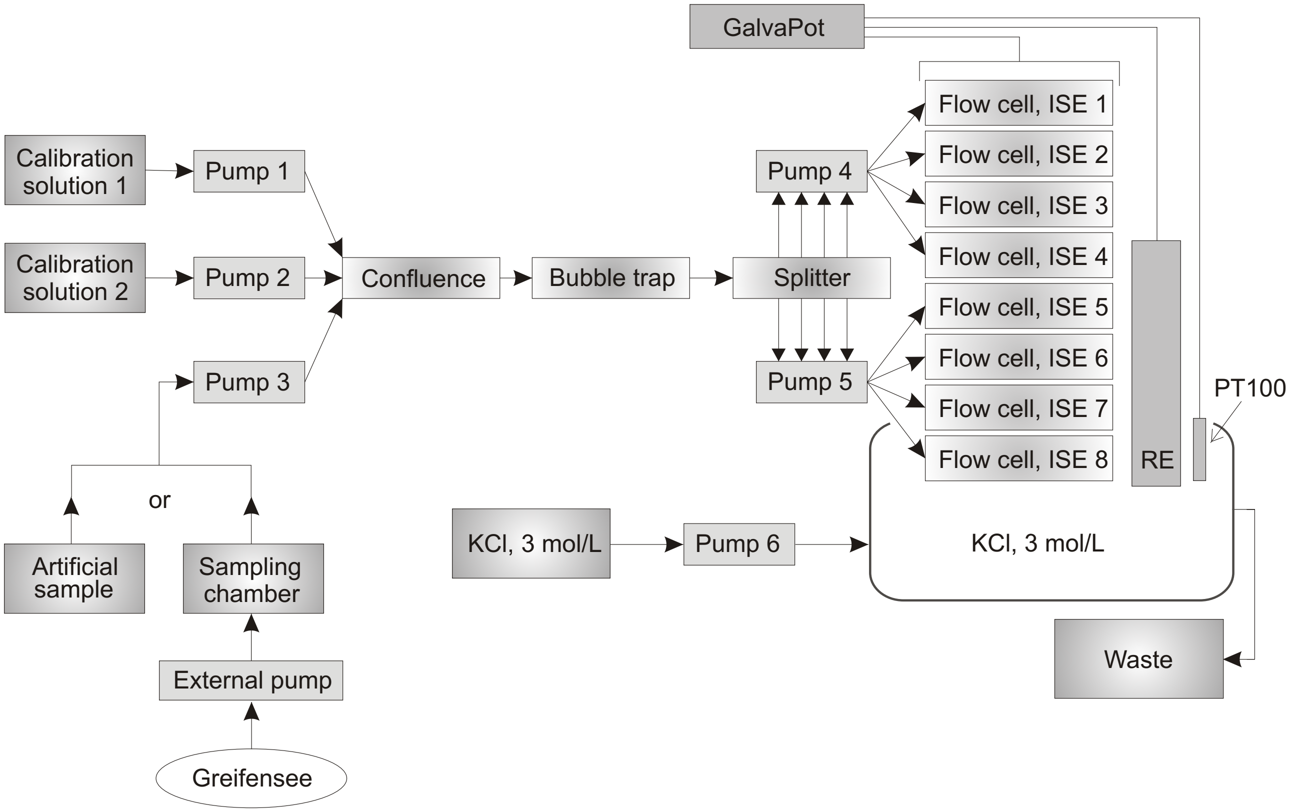

GalvaPot
Calibration solution 1
Pump 1
Calibration solution 2
Pump 2
Confluence
Bubble trap
Splitter
Pump 3
Pump 4
Pump 5
Flow cell, ISE 1
Flow cell, ISE 2
Flow cell, ISE 3
Flow cell, ISE 4
Flow cell, ISE 5
Flow cell, ISE 6
Flow cell, ISE 7
Flow cell, ISE 8
RE
PT100
or
Artificial sample
Sampling chamber
External pump
Greifensee
KCl, 3 mol/L
Pump 6
KCl, 3 mol/L
Waste

Figure S6

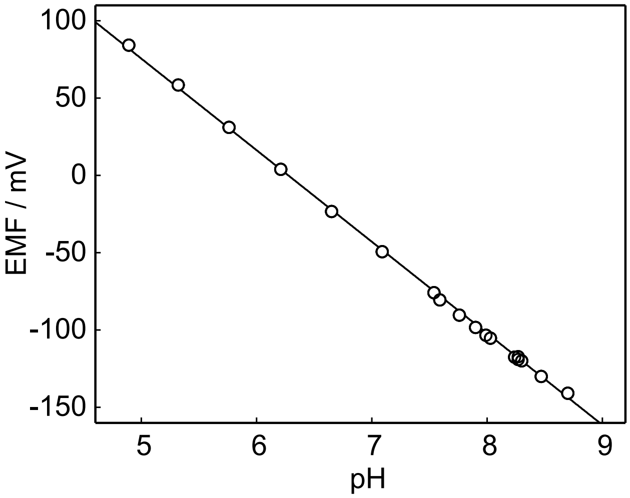


Figure S7

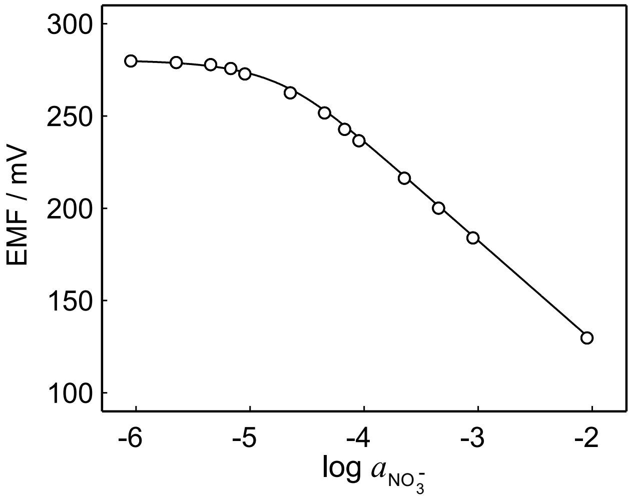


Figure S8

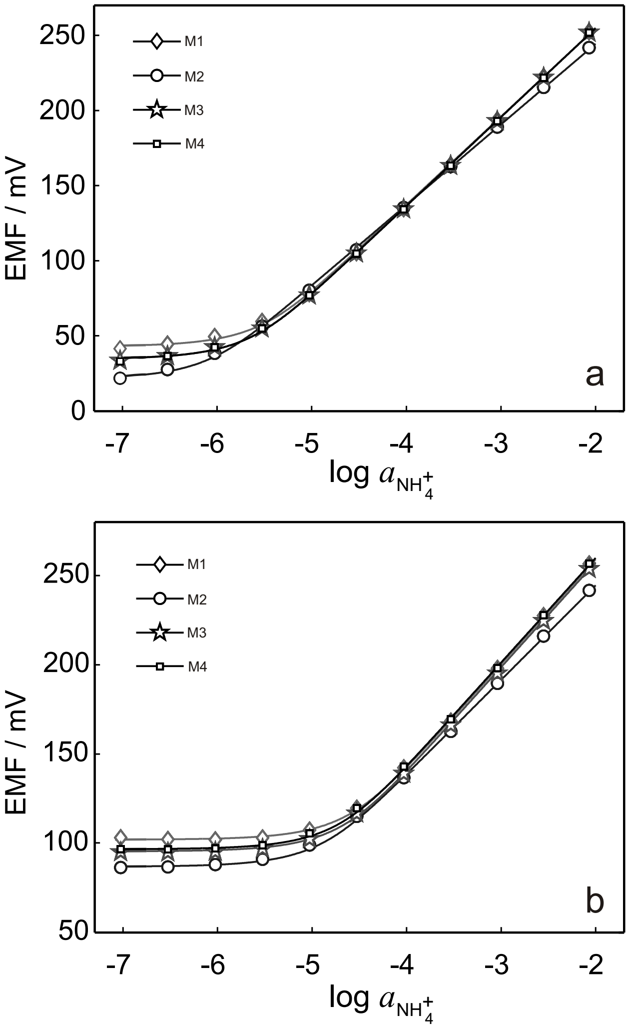

M1
M2
M3
M4
EMF / mV
250
200
150
100
50
0
-7
-6
-5
-4
-3
-2
log $a_{NH_4^+}$
a
M1
M2
M3
M4
EMF / mV
250
200
150
100
50
-7
-6
-5
-4
-3
-2
log $a_{NH_4^+}$
b

Figure S9

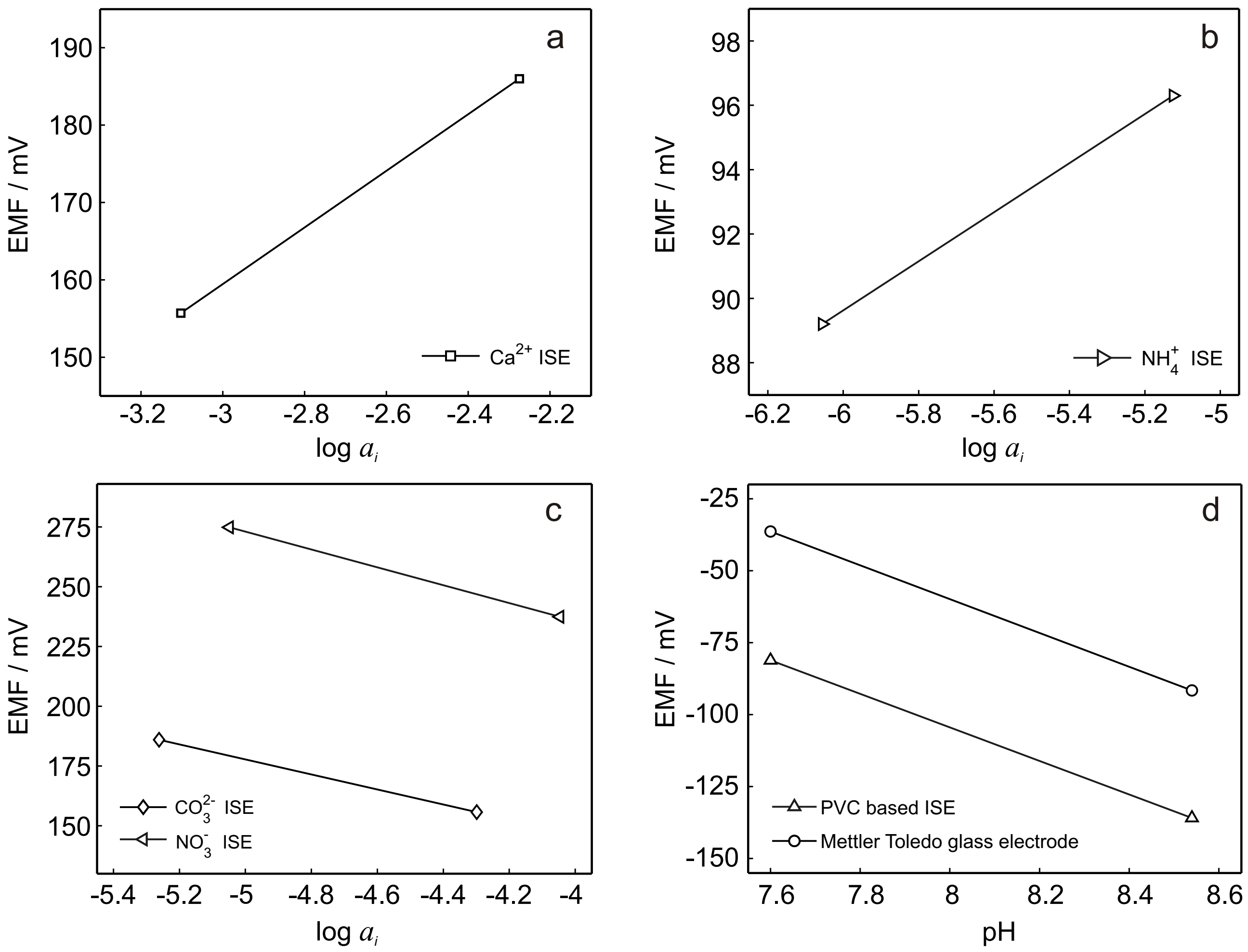
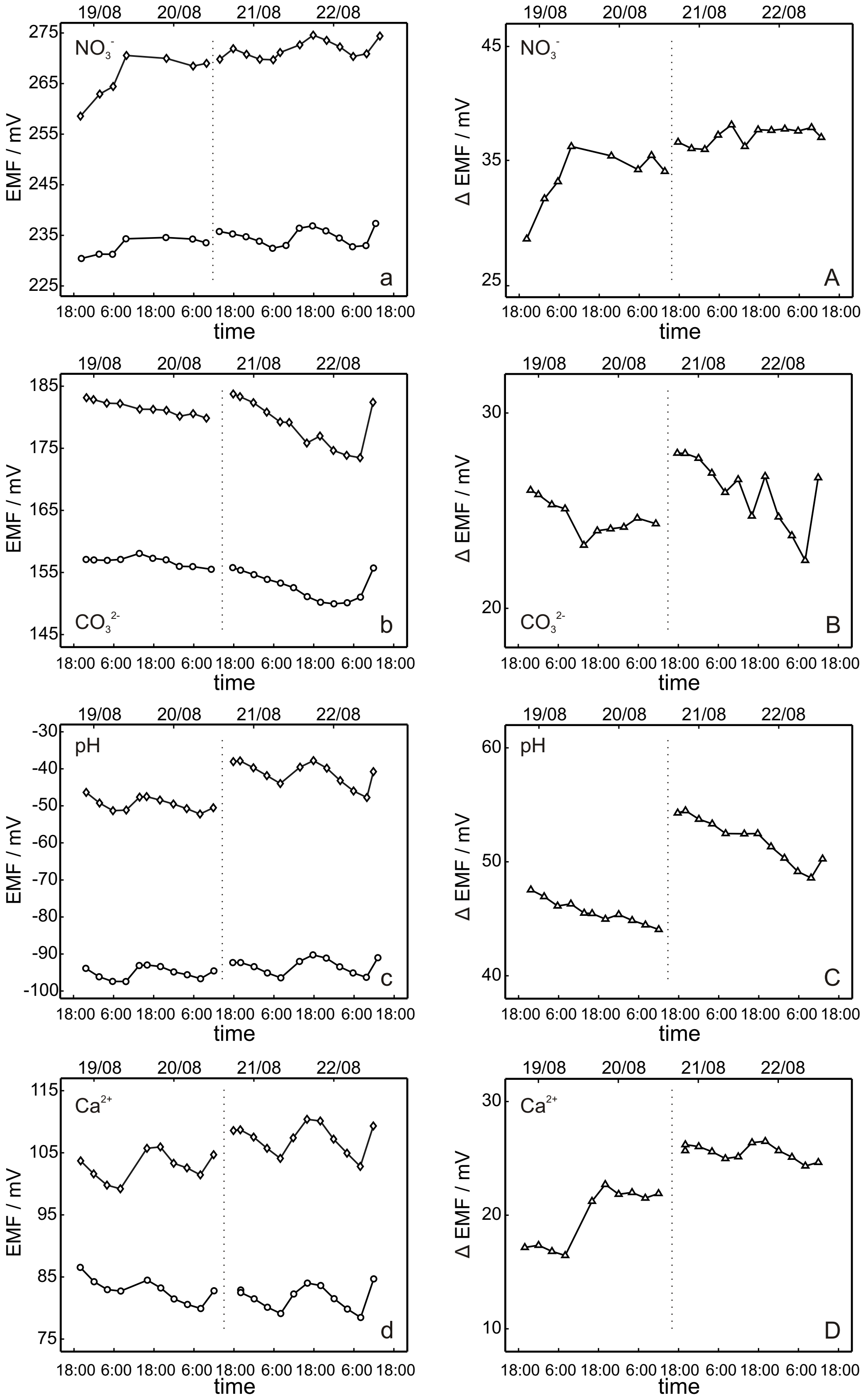

a
EMF / mV
190
180
170
160
150
$Ca^{2+}$ ISE
-3.2
-3
-2.8
-2.6
-2.4
-2.2
log $a_i$
b
EMF / mV
98
96
94
92
90
88
$NH_4^+$ ISE
-6.2
-6
-5.8
-5.6
-5.4
-5.2
-5
log $a_i$
c
EMF / mV
275
250
225
200
175
150
$CO_3^{2-}$ ISE
$NO_3^-$ ISE
-5.4
-5.2
-5
-4.8
-4.6
-4.4
-4.2
-4
log $a_i$
d
EMF / mV
-25
-50
-75
-100
-125
-150
PVC based ISE
Mettler Toledo glass electrode
7.6
7.8
8
8.2
8.4
8.6
pH

Figure S10


19/08
20/08
21/08
22/08
NO$_3^-$
CO$_3^{2-}$
pH
Ca$^{2+}$
EMF / mV
Δ EMF / mV
275
265
255
245
235
225
45
35
25
185
175
165
155
145
30
20
-30
-40
-50
-60
-70
-80
-90
-100
60
50
40
115
105
95
85
75
10
18:00
6:00
time
a
A
b
B
c
C
d
D