Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts.

Supporting Information for:

Submersible Probe with In-line Calibration and Symmetrical Reference Element for Continuous Direct Nitrate Concentration Measurements

Tara Forrest [a], Thomas Cherubini [a], Stéphane Jeanneret [a], Elena Zdrachek [a], Polyxeni Damala [a], Eric Bakker [a]

[a] Department of Inorganic and Analytical Chemistry, University of Geneva, Quai Ernest-Ansermet 30, CH-1211 Geneva, Switzerland

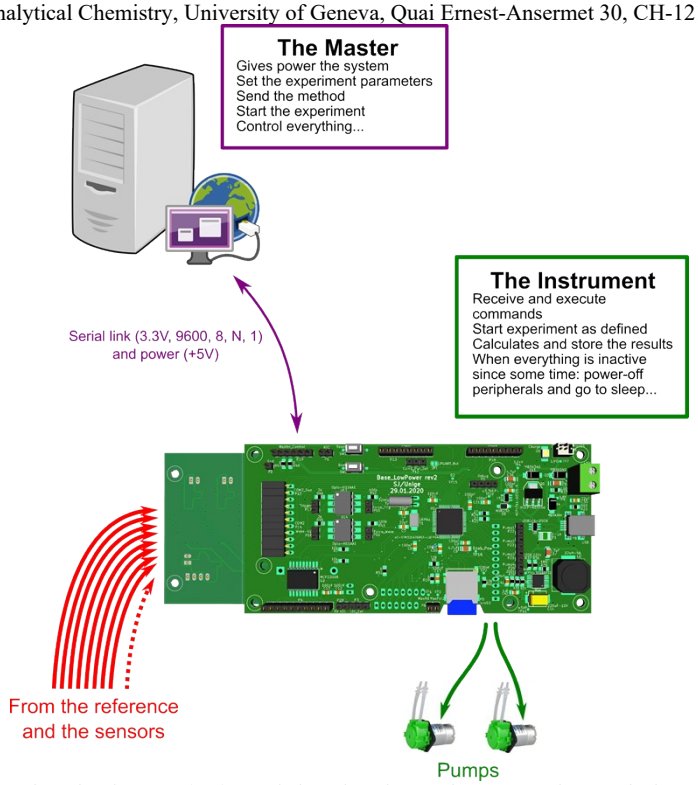

Figure S1 : Scheme of main board controlling the probe. The Master (user) controls the probe and sets up the experiment that is run by the instrument. Through commands the instrument activates pump and executes different operations

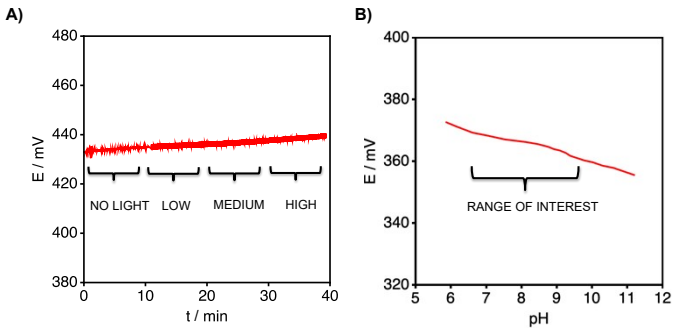

Figure S2 : A) Response of nitrate-selective electrode in 1 mM $NaNO_3$ subjected to different light intensities. The signal was fist measured in full darkness (no light) and then LED lights were turned on at different intensities: 563 LM (low) – 1126 LM (medium) – 1690 LM (high). B) Response of nitrate-selective electrode in 1 mM $NaNO_3$ while varying the pH. 1 M H_2SO_4 was first spiked into the solution to reach an acidic pH and then 0.1 M NaOH was gradually added to reach a basic pH.

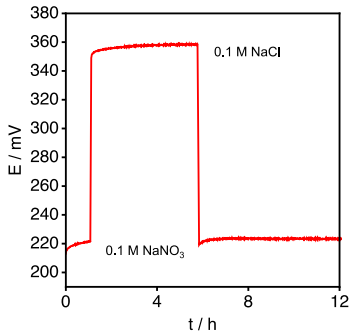

Figure S3 : Response of nitrate-selective electrode in 0.1 M $NaNO_3$ for 1h followed by immersion in 0.1 M NaCl for 6h. The electrodes were then again immersed in 0.1 M $NaNO_3$ to check the signal recovery. No water layer formation could be observed during the testing period.

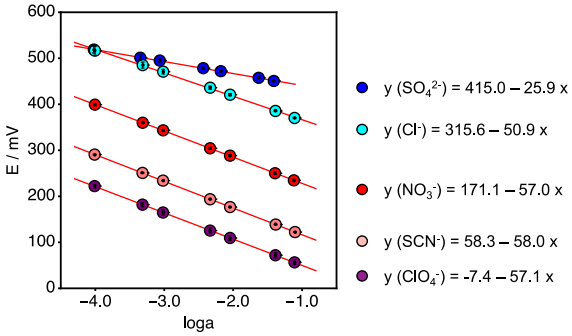

Figure S4 : Potentiometric response of electrode for several anions. The selectivity experiment was performed according to the MSSM, where calibrations were performed sequentially according to the lipophilicity of the anions. From top to bottom, potentiometric response towards: Na_2SO_4 (blue), NaCl (cyan), $NaNO_3$ (red), NaSCN (pink) and $NaClO_4$ (purple).

Table S1 : Calculated selectivity coefficients from Figure S4.

Primary Ion	Interfering Ion	$\log K_{ij}^{Pot}$	K_{ij}^{Pot}
NO_3^-	SO_4^{2-}	-8.38	$4.13 \cdot 10^{-9}$
	Cl^-	-2.48	$3.27 \cdot 10^{-3}$
	SCN^-	1.94	$8.68 \cdot 10^{1}$
	$ClO4^-$	3.07	$1.17 \cdot 10^{3}$

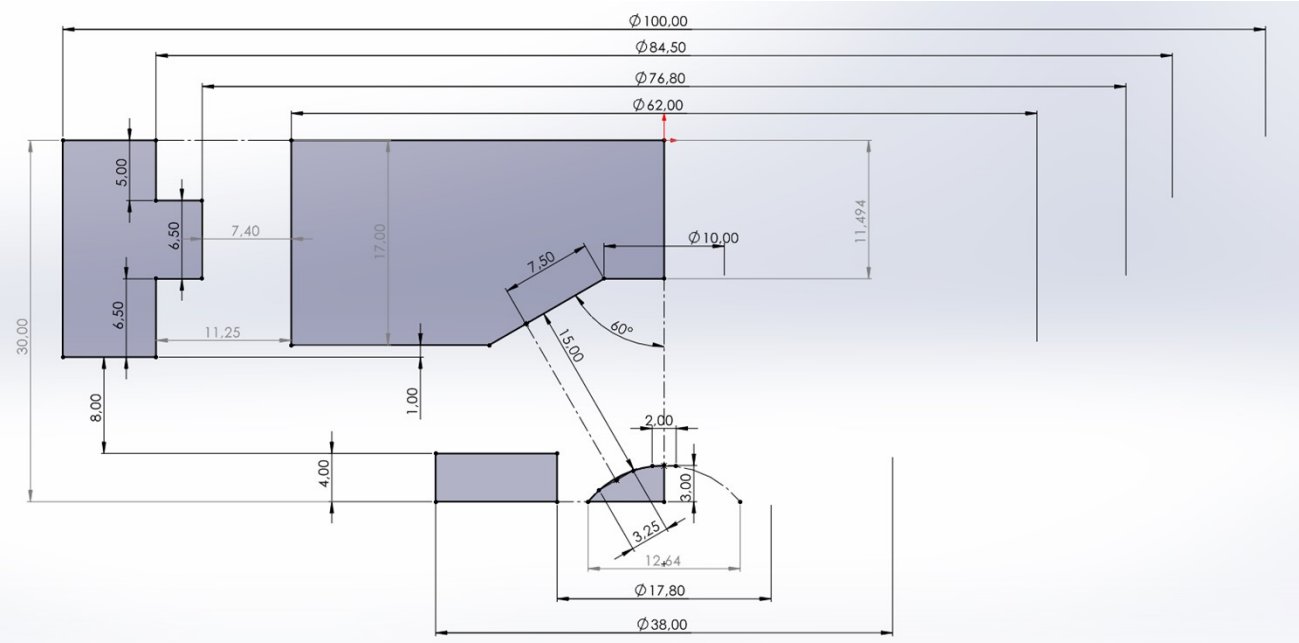

Figure S5 : Schematic side cut of sensing dome and its housing. The dimension are given in mm.

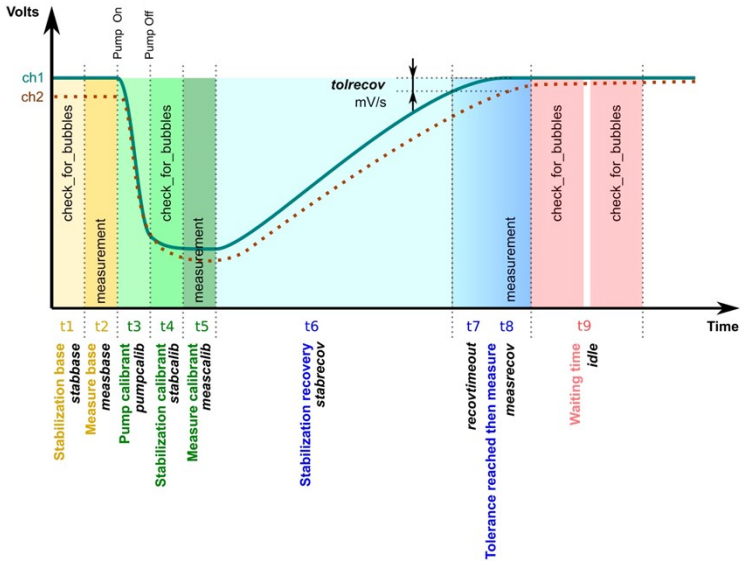

Figure S6 : Preprogrammable calibration routine. All timed events (t1 – t9) can be determined individually to customise the protocol to the adequate length and their description can be found in Table S5

Table S2 : Concentrations of all major ions in Rhône River sample with determination method

Ion	Method	Concentration [M]
Cl^-	Ion Chromatography	$2.76 \cdot 10^{-4}$
NO_3^-	Ion Chromatography	$3.53 \cdot 10^{-5}$
SO_4^{2-}	Ion Chromatography	$4.76 \cdot 10^{-4}$
HCO_3^-	Titration	$9.37 \cdot 10^{-4}$
Na^+	Atomic Emission Spectroscopy	$2.86 \cdot 10^{-4}$
K^+	Atomic Emission Spectroscopy	$6.18 \cdot 10^{-5}$
Ca^{2+}	Atomic Absorption Spectroscopy	$1.10 \cdot 10^{-3}$
Mg^{2+}	Atomic Absorption Spectroscopy	$2.34 \cdot 10^{-4}$

Table S3 : Nitrate potentiometric response in Rhône River water sample. Potential values for raw sample and spiked sample (calibrant) recorded during tank-based experiment versus symmetrical nitrate reference.

Cycle	1	2	3	4	5	6	7	Average	StDev
Sample potential value [mV]	2.92	2.75	2.42	2.67	2.79	2.74	2.63	2.70	0.16
Calibrant potential value [mV]	-37.70	-34.07	-34.26	-34.26	-34.42	-34.51	-34.80	-34.30	0.35
Δ EMF [mV]	36.62	36.82	36.93	36.93	37.21	37.25	37.43	37.01	0.29

Table S4 : Nitrate potentiometric response in Rhône River water sample. Potential values for raw sample and spiked sample (calibrant) recorded during tank-based experiment versus Ag/AgCl reference electrode.

Cycle	1	2	3	4	5	6	7	Average	StDev
Sample potential value [mV]	34.16	33.20	34.70	34.52	34.41	34.74	33.63	34.19	0.58
Calibrant potential value [mV]	-1.00	-0.50	0.30	0.23	-0.38	-0.48	-1.77	-0.60	0.63
Δ EMF [mV]	35.16	33.70	35.00	34.29	34.79	35.22	35.40	34.79	0.60

Table S5 : Description of timed event during calibration routine presented in Figure S6

Timed event	Name	Function
t1	Stabilisation base	Initial time at the beginning of the cycle set to leave time to the signal to stabilise
t2	Measure base	Measurement of the signal to have a potential value before the calibrant
t3	Pump calibrant	Activation of calibrant pump. t3 will stop when t5 is over
t4	Stabilisation calibrant	Time to have stabilisation of the calibrant signal
t5	Measure calibrant	Measurement of the signal to have a potential value of the calibrant. This value will be stored internally during the cycle to calculate the analyte concentration of the sample. Pump is stopped at the end of t5.
t6	Stabilisation recovery	Gradual signal recovery. The sample slowly replaces the calibrant solution inside the sensing dome.
t7	Recovery Timeout	Correlates the current signal value with the one obtained in t2 to estimate if the calibrant solution has been fully replaced
t8	Measure Recovery	
t9	Waiting time	Records the measuring electrodes signal at fixed interval to have time based potential reading and concentration values.

Table S6 : Concentrations of nitrate determined by ion chromatography (n=3)

Time [min]	Concentration [M]
50	$4.093 \pm 0.023 \cdot 10^{-5}$
1160	$3.491 \pm 0.005 \cdot 10^{-5}$
1400	$3.583 \pm 0.004 \cdot 10^{-5}$
1550	$3.854 \pm 0.005 \cdot 10^{-5}$
2690	$3.846 \pm 0.004 \cdot 10^{-5}$
4490	$3.858 \pm 0.005 \cdot 10^{-5}$

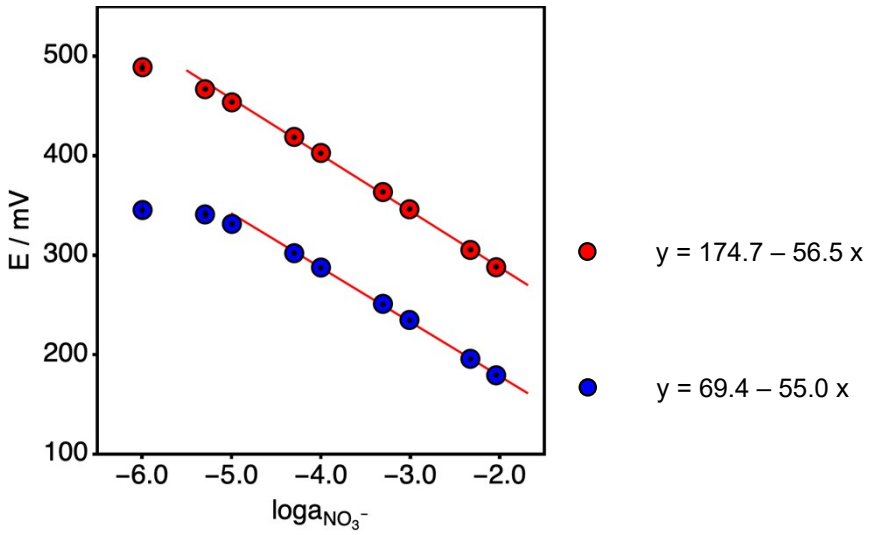

Figure S7 : Potentiometric response of same nitrate-selective electrode versus double-junction reference electrode before immersion in real sample (red trace) and after 75h immersion in real sample (blue trace). Error bars represent standard deviation (n=3).