Electronic Supplementary Material (ESI) for Analytical Methods.

Electronic Supporting Information

for

A novel all-3D-printed thread-based microfluidic device with embedded electrochemical detector: first application on environmental analysis of nitrite

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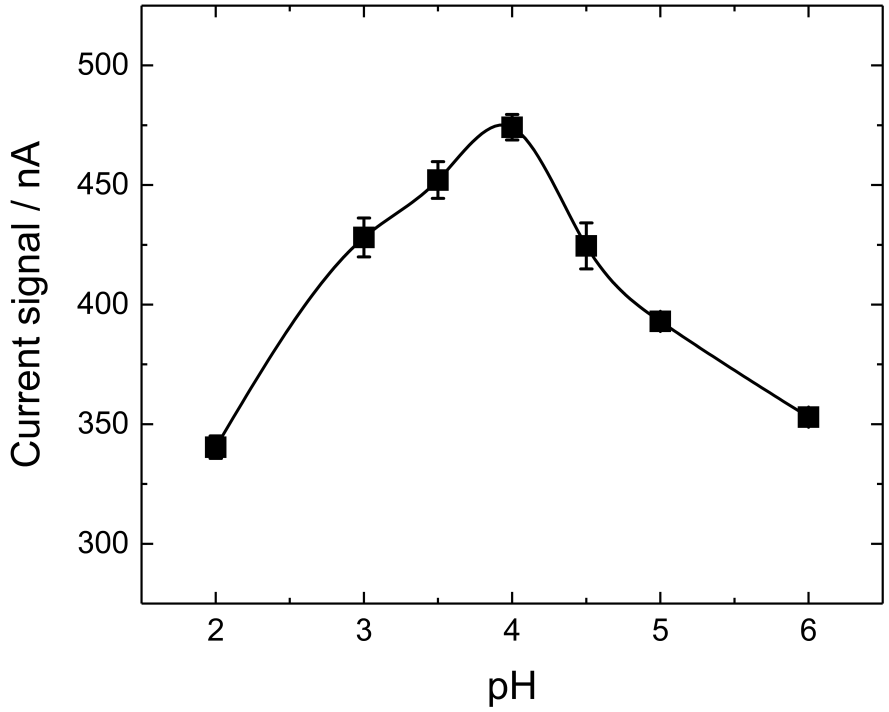

Figure S1: Effect of the pH on the intensity of the chronoamperometric signal of 50 μmol L^{-1} nitrite standard. The measurements were carried out in a media composed of 0.1 mol L^{-1} BR buffer. Conditions: detection potential was +0.90 V, time interval was 0.1 s and injected volume was 5.0 μL. Results for n = 3 measurements.

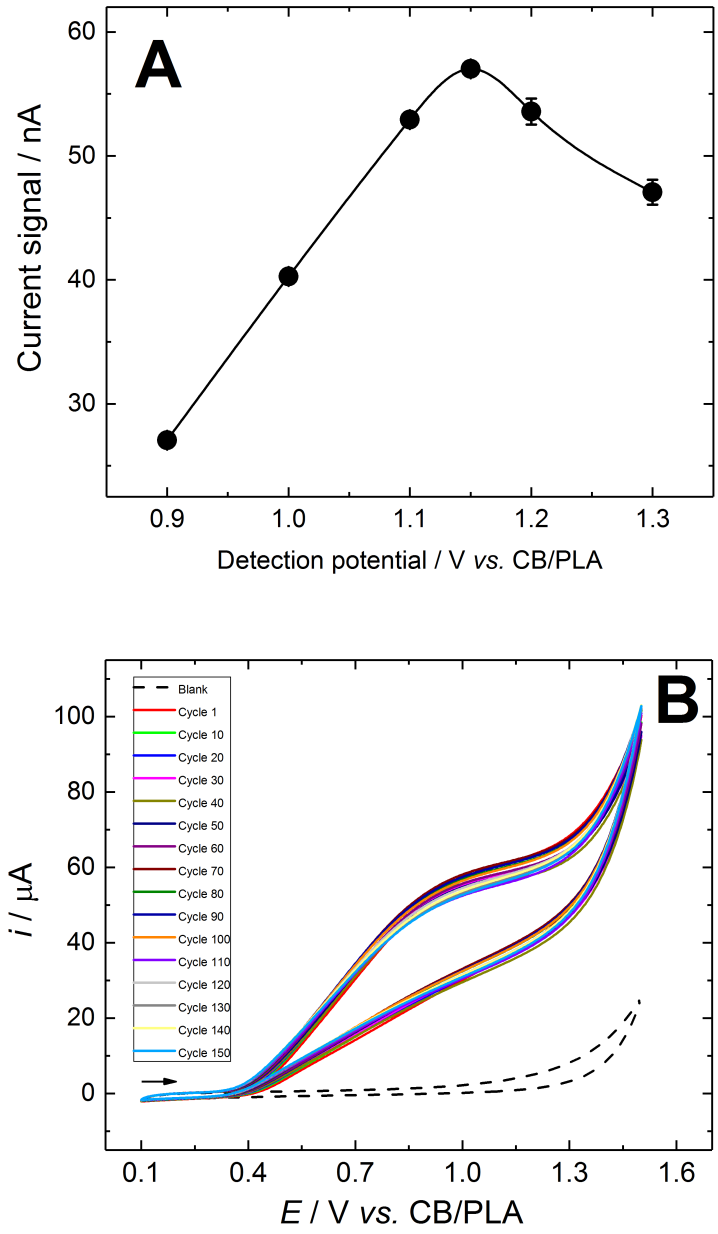

Figure S2: A) variation on the chronoamperometric response of 10 µmol L^{-1} nitrite standard as a function of detection potential. The time interval was 0.1 s and the injected volume was 5.0 µL. Results for $n = 3$ measurements; B) consecutive cyclic voltammograms ($n = 150$ cycles) recorded with the embedded 3D-printed CB/PLA electrochemical detector in the presence (solid lines) and absence (dashed line) of 1.5 mmol L^{-1} nitrite standard. The scan rate was 100 mV s^{-1}. All measurements were performed in a media composed of 0.1 mol L^{-1} BR buffer (pH = 4.0).

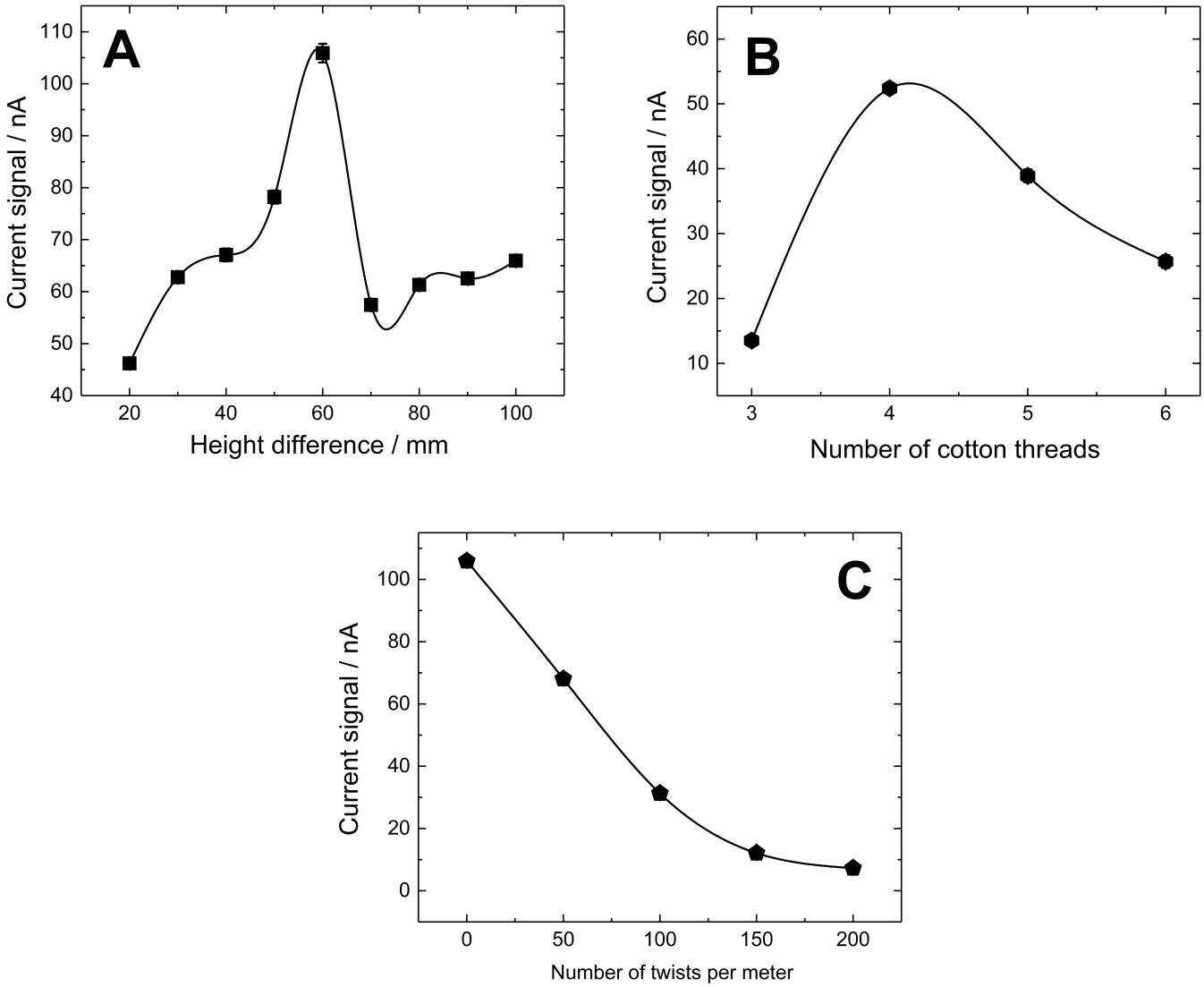

Figure S3: Influence of the height difference between the inlet and outlet reservoirs (A), amount of threads in the microfluidic channel (B) and number of twists per meter (C) in the analytical response of 10 μmol L^{-1} nitrite standard. The chronoamperometric measurements were carried out in a media composed of 0.1 mol L^{-1} BR buffer (pH = 4.0). The time interval was 0.1 s, the detection potential was +1.15 V and the injection volume was 5.0 μL. Results for n = 3 measurements.

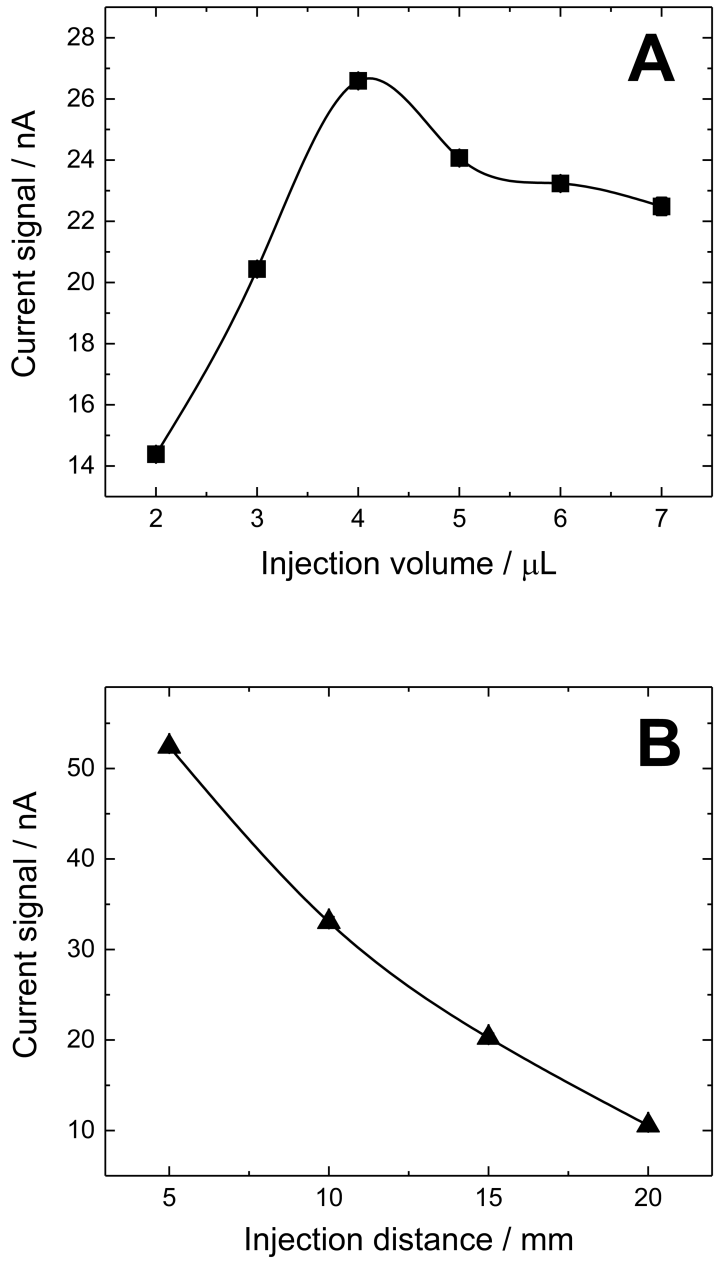

Figure S4: Dependence of the current signal of 10 μmol L^{-1} nitrite standard on the injection volume (A) and injection distance (B). Measurements obtained in a media composed of 0.1 mol L^{-1} BR buffer (pH = 4.0). The time interval and the detection potential were 0.1 s and +1.15 V, respectively. Results for n = 3 measurements.

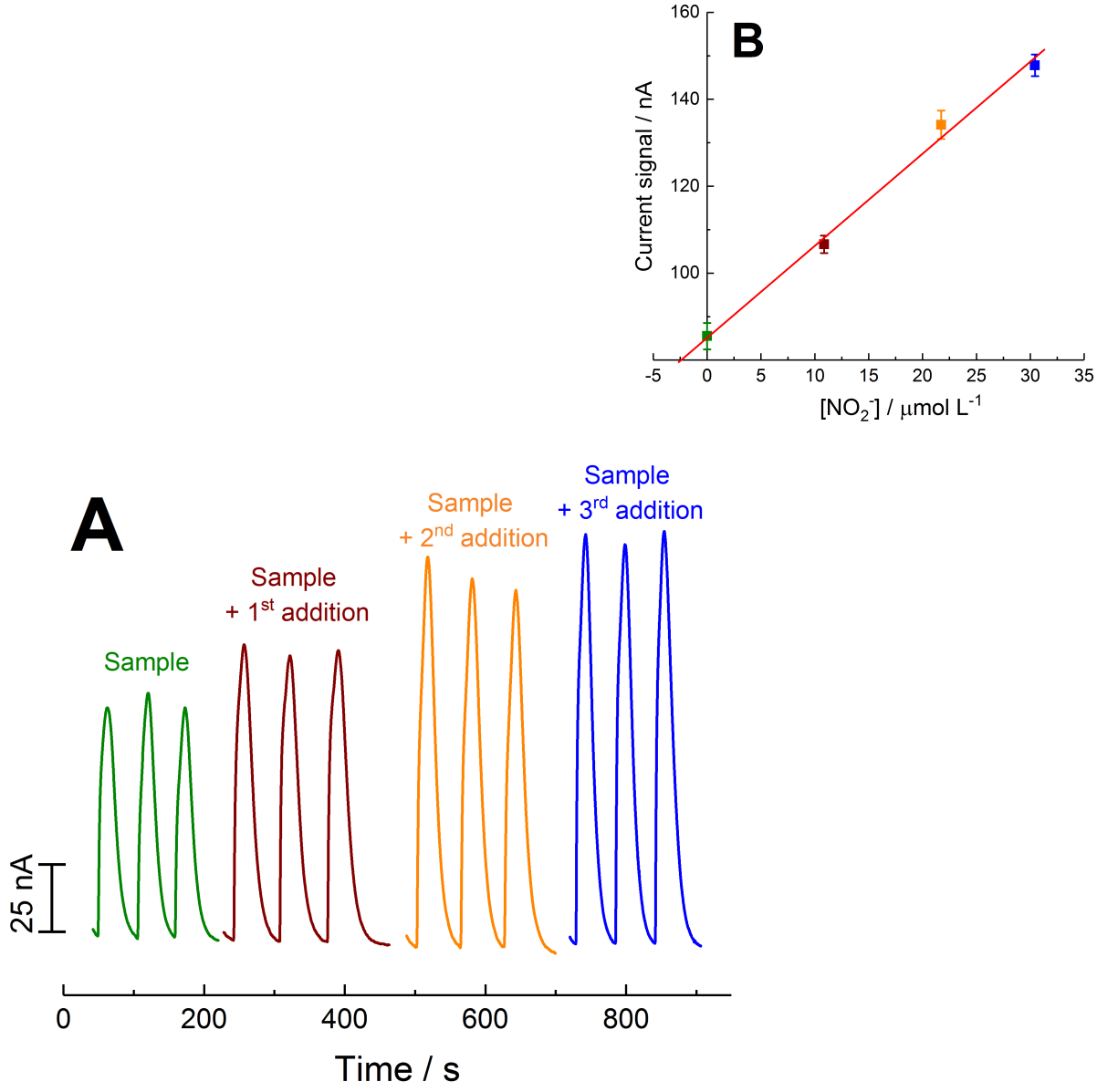

Figure S5: Amperometric measurements (A) and respective standard addition curve (B) obtained during one of the determinations of nitrite in the well water samples. The points in the standard addition curve are the average of $n = 3$ measurements. Other conditions: see Table S1 (ESI).

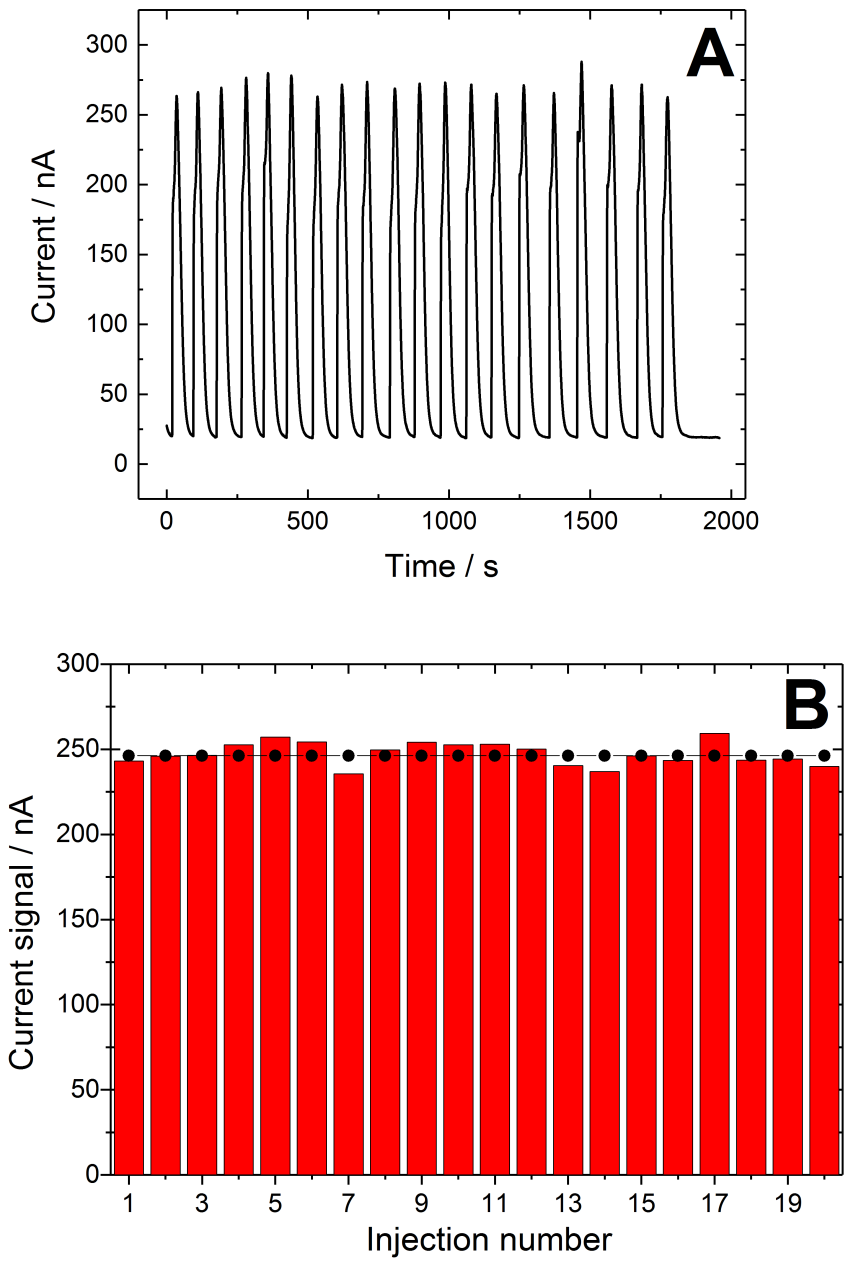

Figure S6: Amperometric response for n = 20 successive injections of 50 µmol L^{-1} nitrite standard (A). Experimental conditions: see Table S1 (ESI); Plot of the current signals used for calculation of the *RSD* (B). The horizontal line indicates the averaged current.

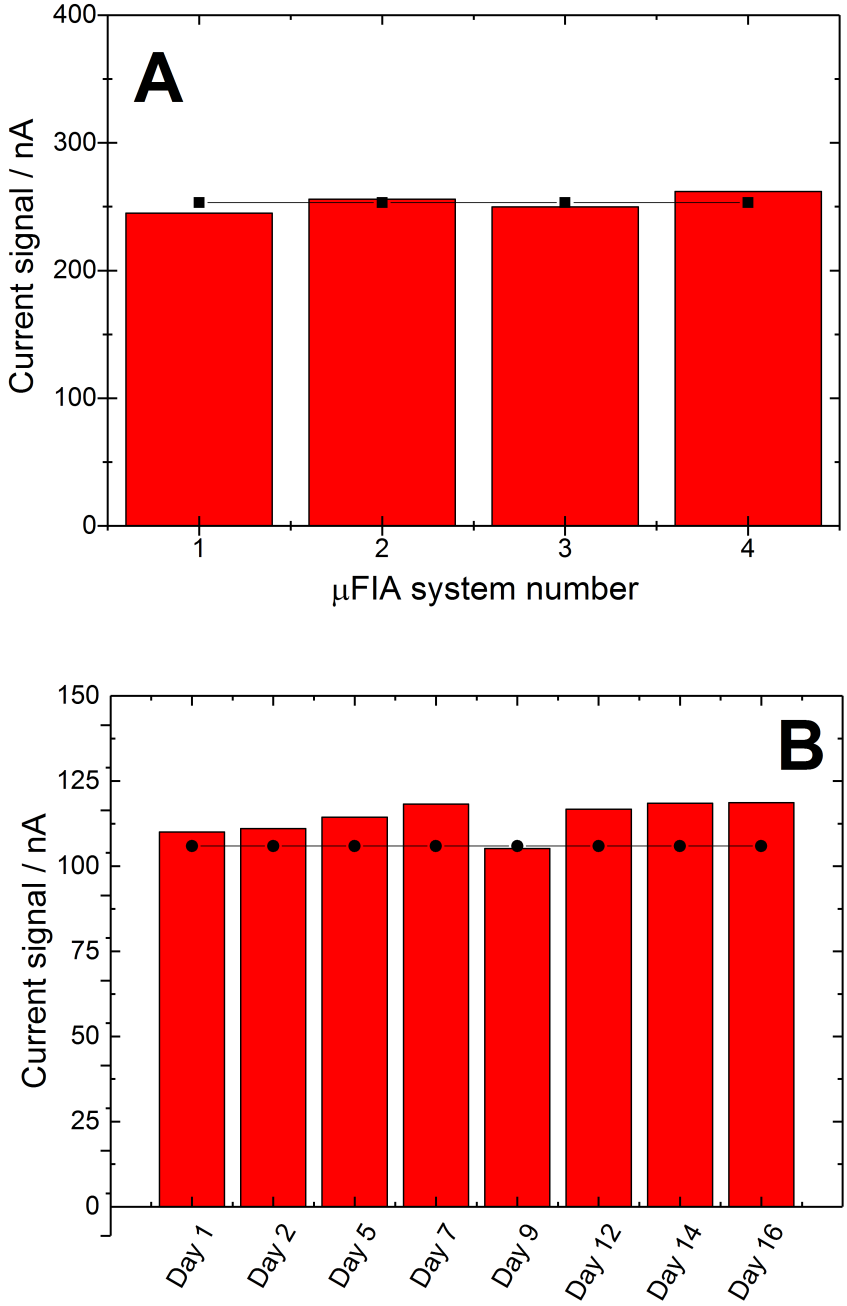

Figure S7: Results for the inter-electrode reproducibility (A) and stability (B) studies. A 50 μmol L^{-1} nitrite standard solution was used. The horizontal line shows the averaged current Experimental conditions: see Table S1 (ESI).

Table S1: Experimental and instrumental parameters investigated regarding the analytical sensing of nitrite using the fully 3D-printed μTED with the embedded CB/PLA electrochemical detector.

Parameter	***Range studied***	***Optimum value***
pH	2.0 to 6.0	4.0
Detection potential	+0.90 to +1.30 V	+1.15 V
Height difference	20 to 100 mm	60 mm
Number of cotton threads	3 to 6	4
Number of twists	0 to 200 per meter	0 (threads not twisted)
Injection volume	2.0 to 7.0 μL	4.0 μL
Injection distance to detector	5 to 20 mm	5 mm

Table S2: Results of the study carried out to assess the selectivity of nitrite electrochemical response regarding some species typically present in natural waters.

Interferent species	**Ratio nitrite/interferent**	**Nitrite relative response [1] (%)**	***RSD* [2] (%)**
NO_3^-	1/100	99.2	2.2
SO_4^{2-}	1/100	98.5	4.1
Cl^-	1/100	98.8	3.4
PO_4^{3-}	1/100	100.4	2.7
F^-	1/100	101.2	1.6
K^+	1/100	99.0	2.5
Na^+	1/100	96.5	3.1
Mg^{+2}	1/100	102.3	4.0
Mn^{+2}	1/10	103.6	3.7
Fe^{+3}	1/10	95.4	2.8
Pb^{+2}	1/10	98.1	1.4
Cu^{+2}	1/10	103.6	2.3
Co^{+2}	1/10	97.8	4.4
Cd^{+2}	1/10	96.9	1.9
Zn^{+2}	1/10	103.4	3.2

[1] (Nitrite response in presence of interferent/nitrite response in absence of interferent) ×100%

[2] Results for $n = 3$ measurements. Experimental conditions: see Table S1.