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Sensors for Sustainable AgriFood & the Environment

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Coláiste na hOllscoile Corcaigh

Rialtas na hÉireann Government of Ireland
Tionscadal Éireann Project Ireland 2040
Ireland's European Structural and Investment Funds Programmes 2014-2020
Co-funded by the Irish Government and the European Union
European Union European Structural and Investment Funds

Why AgriFoods? Societal Impact

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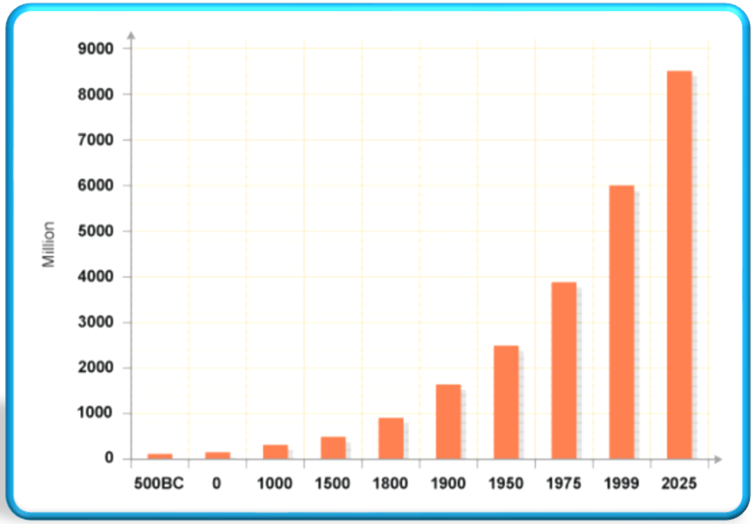
Motivation: Food Production +70% by 2050



SUSTAINABLE DEVELOPMENT GOALS

The Nitrates Directive

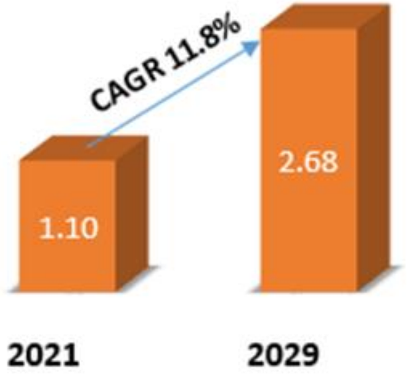
Water Framework Directive
The way towards healthy waters

Climate Change

Competition for land

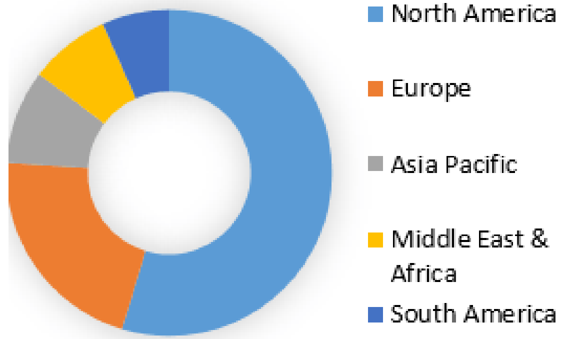
Loss of Biodiversity

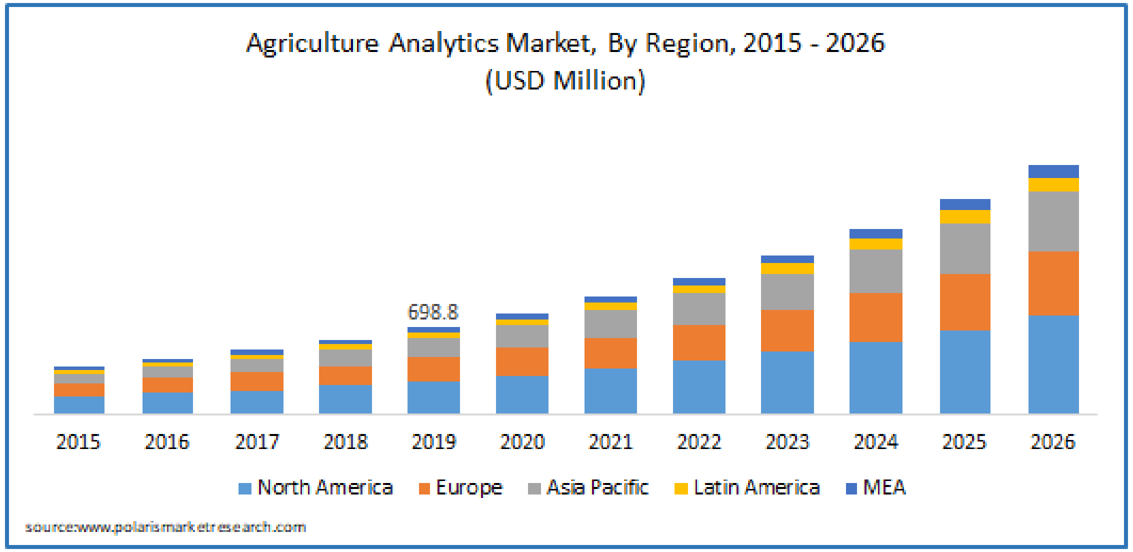
Global Agriculture Analytics Market



Market Size in US$ Billion

Regional Analysis in 2021 (%)





"One of the Key Drivers for market growth is the rising need for accurate crop forecasting and yields."

EU – Green Deal

Reducing nutrient losses and fertiliser use

Existing approach: laboratory based testing

- Farmers are at the coal face – no toolkit
- Monitoring is a costly and timely process
- High cost of ownership / experts required

SAFE Cluster Overview

Sustainable Agri-Foods & the Environment

ICT for Sustainable Agri-Food-Environment

Applications-Focused Research Cluster

SAFE Cluster

Vision

Establish Tyndall as the global deep-tech research institute of choice for development of bio/chemical sensors and systems in Agriculture, Food and the Environment.

Mission Statement

To provide real-time informed decision making capacity to users in animal & plant health; soil; water, air quality.

SAFE Coordinator: Dr Alan O’Riordan

Programme Manager: Dr Gerry Mouzakitis

SAFE Strategic Research Cluster

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- ATOMISTIC & MOLECULAR SIMULATIONS 01
- ADVANCED SENSOR DEVELOPMENT & DEPLOYMENT 02
- SYSTEM MINIATURISATION 03
- SYSTEM INTEGRATION 04
- SYSTEM VALIDATION 05

Teagasc Agriculture and Food Development Authority

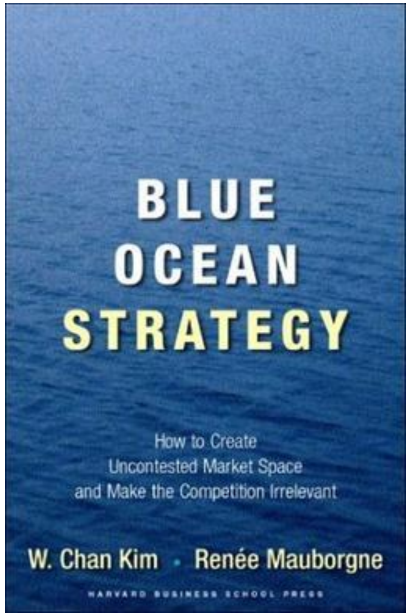
WAGENINGEN UNIVERSITY & RESEARCH

OnePlanet Research Center

SAFE Cluster Strategy

1. Emerging era of Digitalisation in SAFE
2. Research beyond state-of-the-art ICT solutions
3. Identify real world pain points.
4. Collaborate with Agri-Food-Envt experts.

A Leap in value in Agri-Food-Environmental monitoring through beyond state-of-the-art ICT



Approximating Blue Ocean Strategy

Characteristics	SAFE Strategy
Basic Concept align innovation with cost… to create a leap in value… create unexplored new market areas	**SAFE Interpretation** • Utilise beyond state-of-the-art tech • Align outputs to stakeholder needs and cost • Create novel, useful solutions
Differentiation through low cost solutions	• Point-of-use monitoring • No reagents • Tyndall prototypes
Alignment with real needs of customers (stakeholders)	Collaboration with international experts • Real-time monitoring; Not lab-based • Simple: performed by line staff • Data integrity, validation
Create uncontested market space	• Novel sensors & systems Lab-based ➔ Point of use
Exemplars	Novel Sensor & Systems Technology ➢ Real-time nutrient soil monitoring ➢ Water Quality ➢ In-Field disease diagnostics

Research Focus

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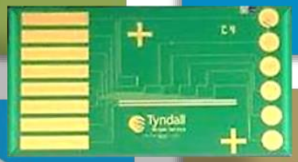
On-Farm Diagnostics
- Diseases
- Animal Health
- Wellbeing & Welfare

Water Quality
- Sterilisation products
- Priority pollutants
- Anthropogenic contamination



Food Security
- Residues

Processing
- Milk Stability
- Milk Content
- Allergens

Plant Pathology
- Real time Virus detection

Soil Chemistry
- Micro & Macro nutrients
- Manure & Dirty Water

- **Developing new advanced nanosensing platforms to digitalize the agri-food sector to enhance food security, reduce losses, increase sustainable production & economic return while also protecting biodiversity.**
- **Digital technologies will transform the traditional based agriculture industry to a knowledge based one.**

Nanosensor Platform

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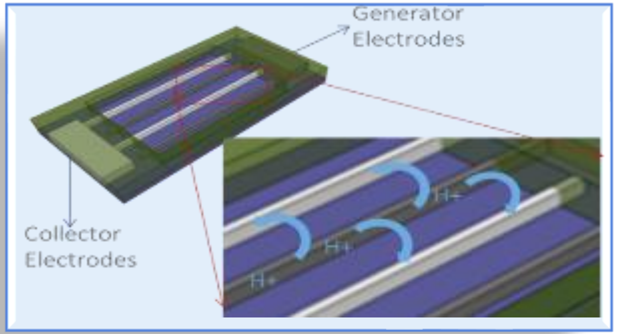
✓ Goal: Develop Sensors & Systems in line with "Do No Significant Harm" principle

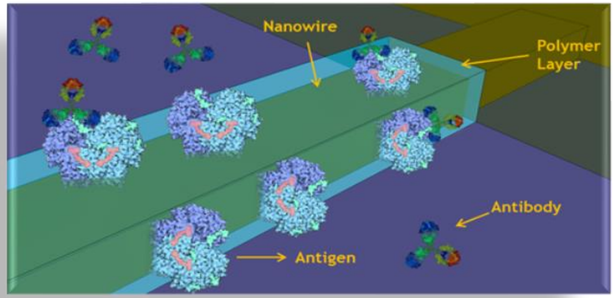
Samples
- Milk
- Blood
- Saliva
- Beverages
- Water
- Soil
- Gases

Electrochemistry



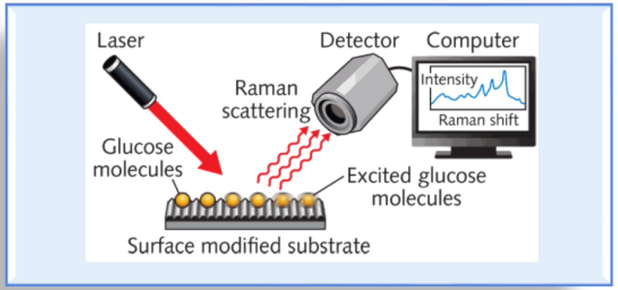
- Generator-Collector
- pH Control
- (Soil) Nutrients
- Electrolytes
- Heavy metals

Bio-electrochemistry



- Parasites
- Viruses
- Proteins
- Biomarkers
- DNA

Surface-Enhanced Raman Scattering



- Food Adulterants
- Flavourings, sweeteners
- Antibiotics
- Pesticides

Electrochemical Nanosensor - Advantages

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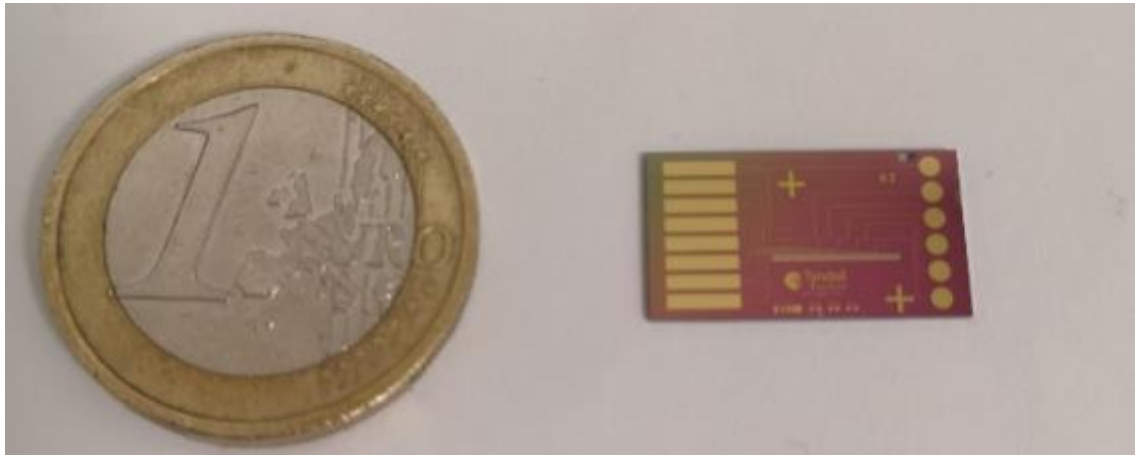
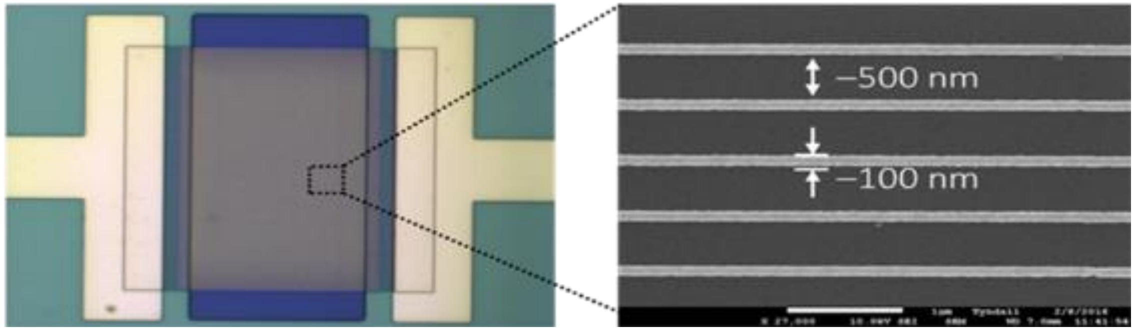


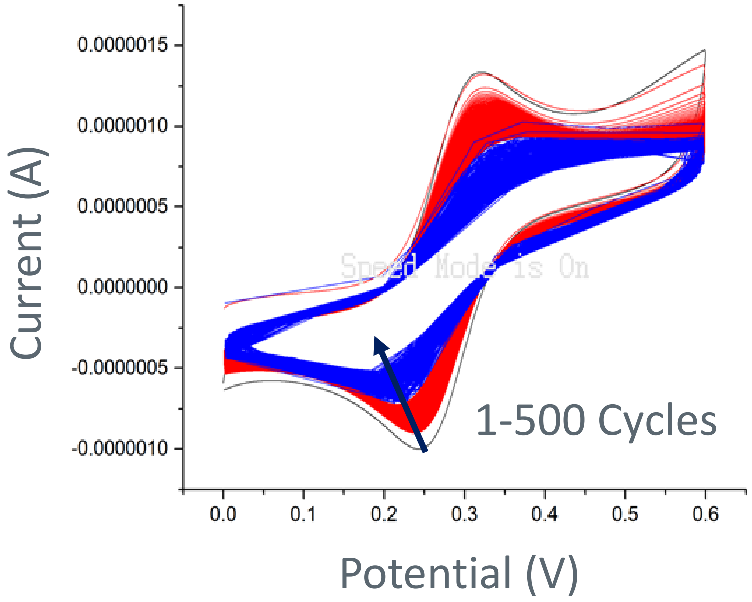


- ✓ On a similar size scale to analyte molecules of interest
- ✓ Demonstrate enhanced sensitivity arising from enhanced analyte mass transport
- ✓ Significantly reduced signal noise (background noise)
- ✓ Can be fabricated at high density (nm separation)
- ✓ Multiplexed detection
- ✓ Enable direct electrical signal readout
- ✓ Very low analyte concentrations
- ✓ Rapid Sensing

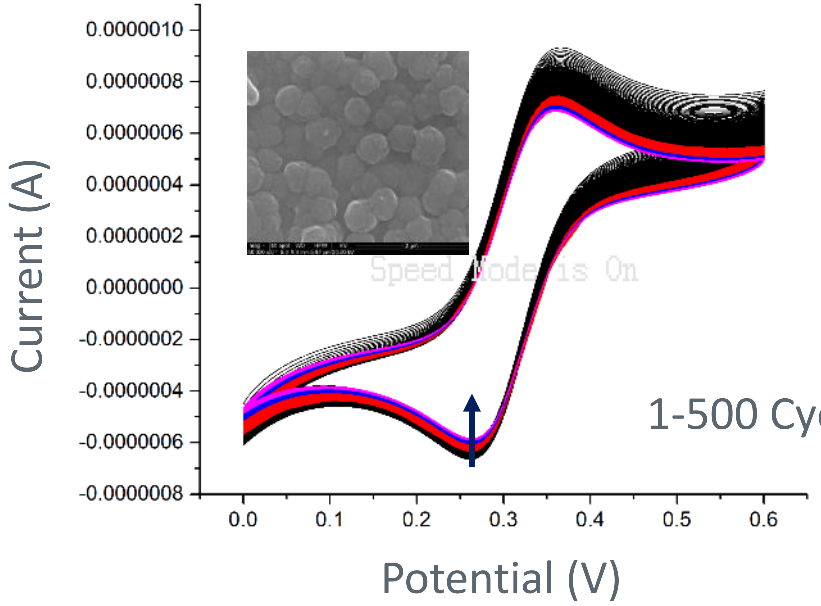
Key Challenges

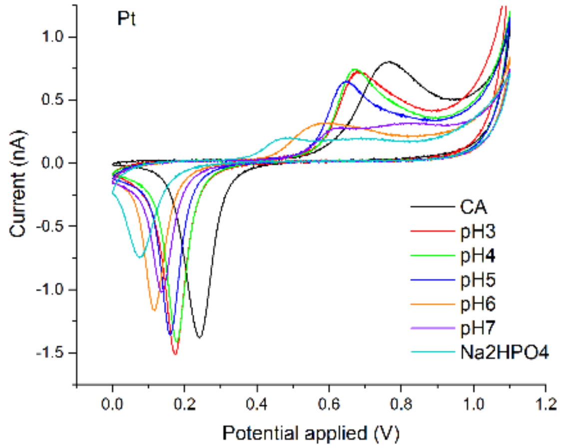
- ➢ Reference electrode drift
- ➢ Specificity requires modification
- ➢ Need to add chemical reagents

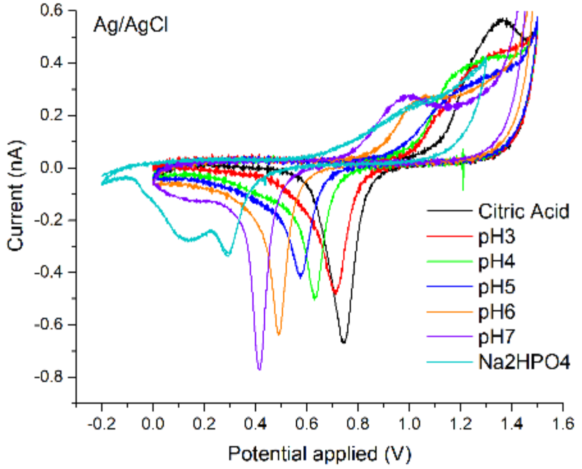
Stabilized Reference Electrode

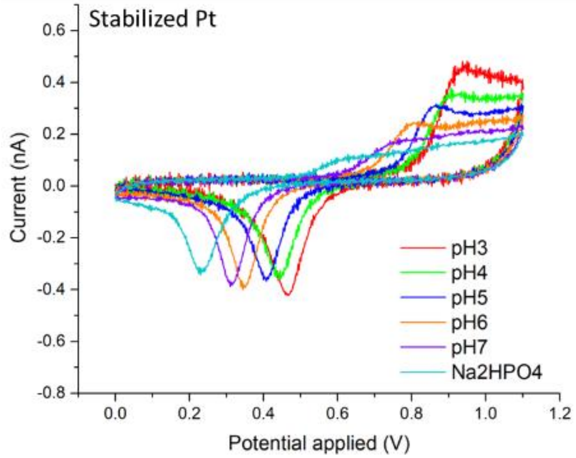


After modification



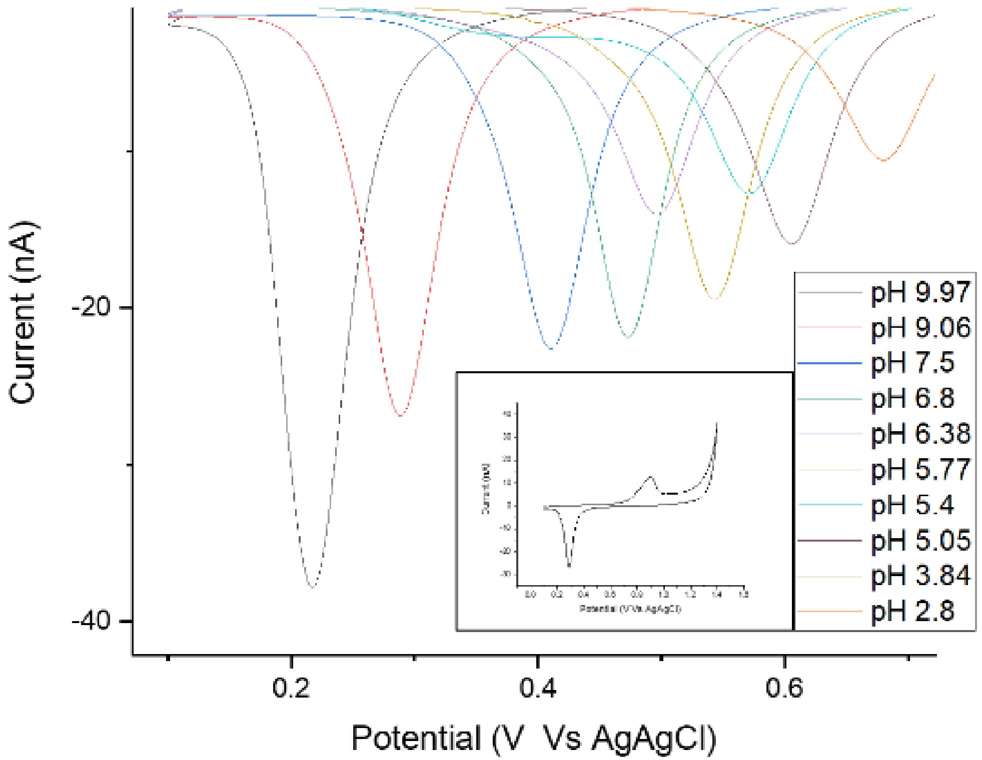


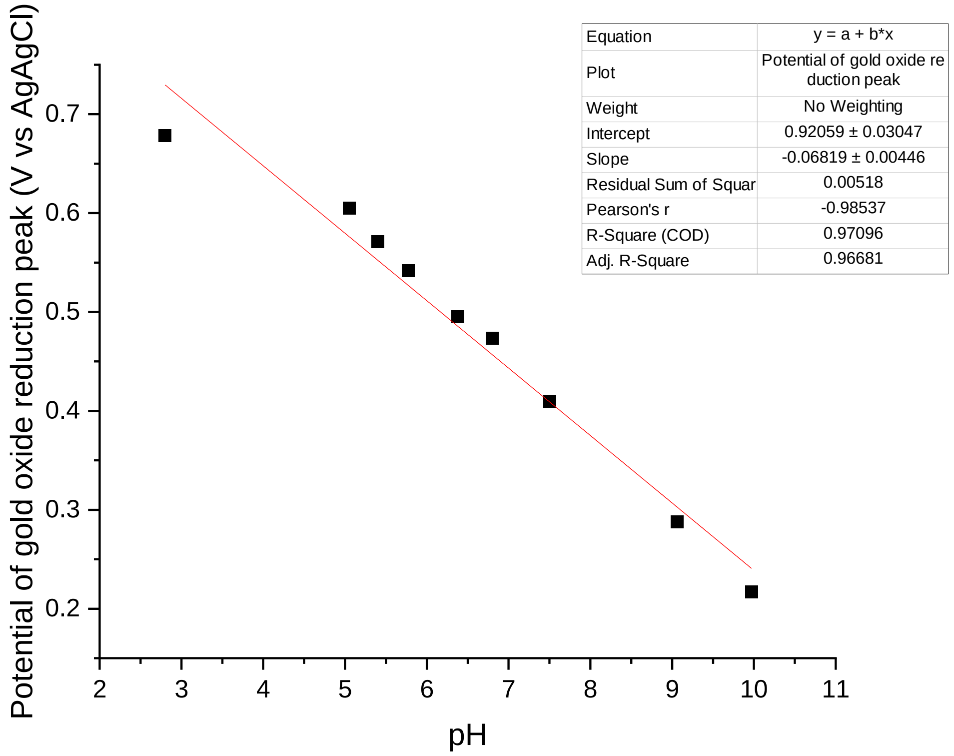




Gold Oxide Reduction as pH Probe

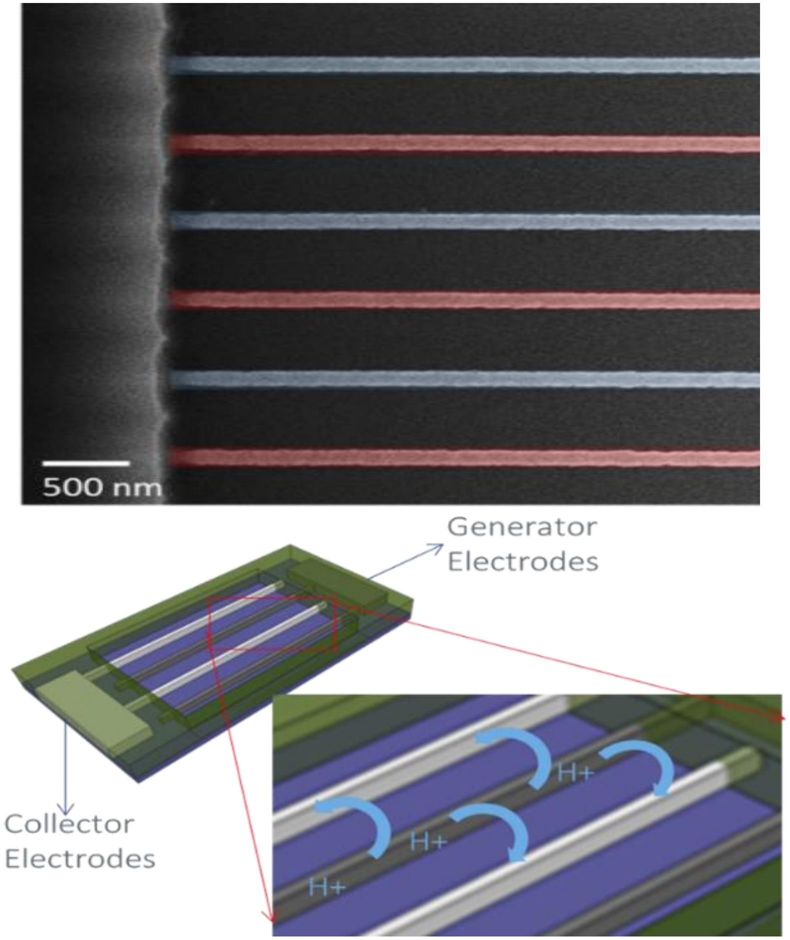
- A gold IDE was used with a 1 µm width electrode and a 2 µm gap
- The electrode was scanned to 1.3 V to generate an oxide, which was subsequently reduced





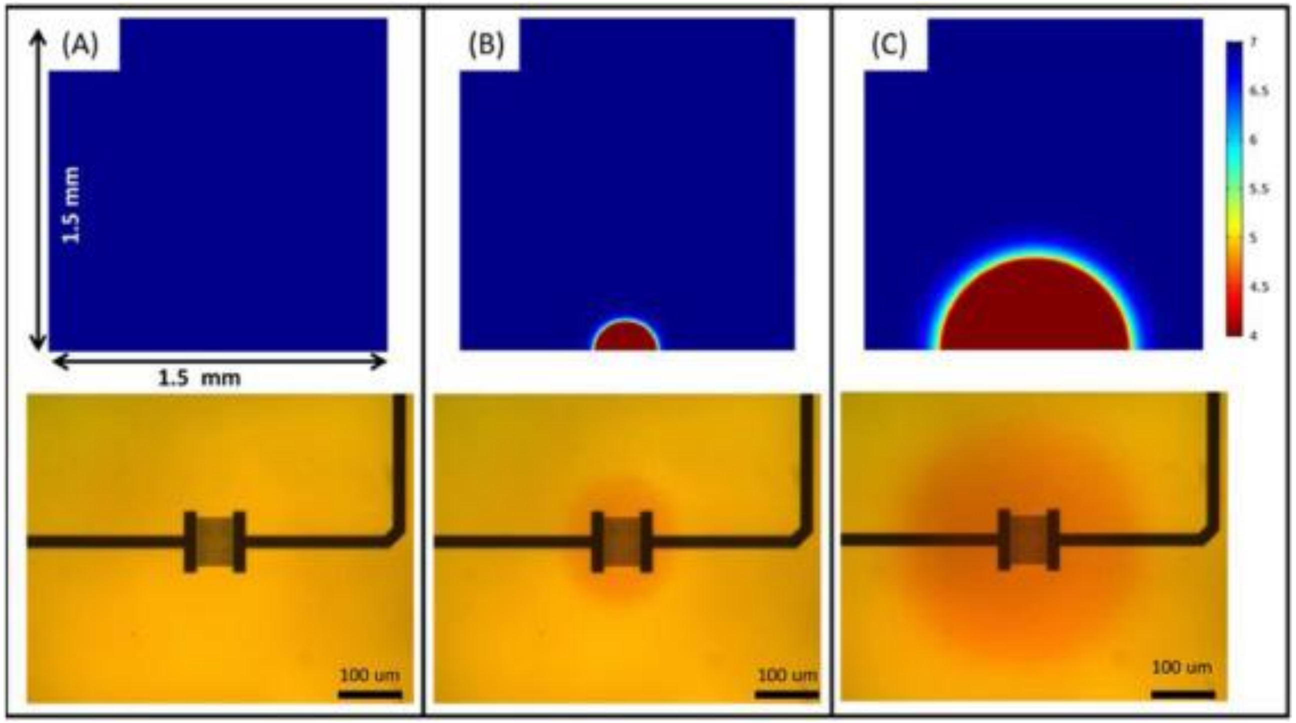
Equation	y = a + b*x
Plot	Potential of gold oxide reduction peak
Weight	No Weighting
Intercept	0.92059 ± 0.03047
Slope	-0.06819 ± 0.00446
Residual Sum of Squar	0.00518
Pearson's r	-0.98537
R-Square (COD)	0.97096
Adj. R-Square	0.96681

Nanoelectrodes – No reagent addition



Simulation of proton diffusion of protons from protonator electrode:

t=0 s t= 1s t=10 s

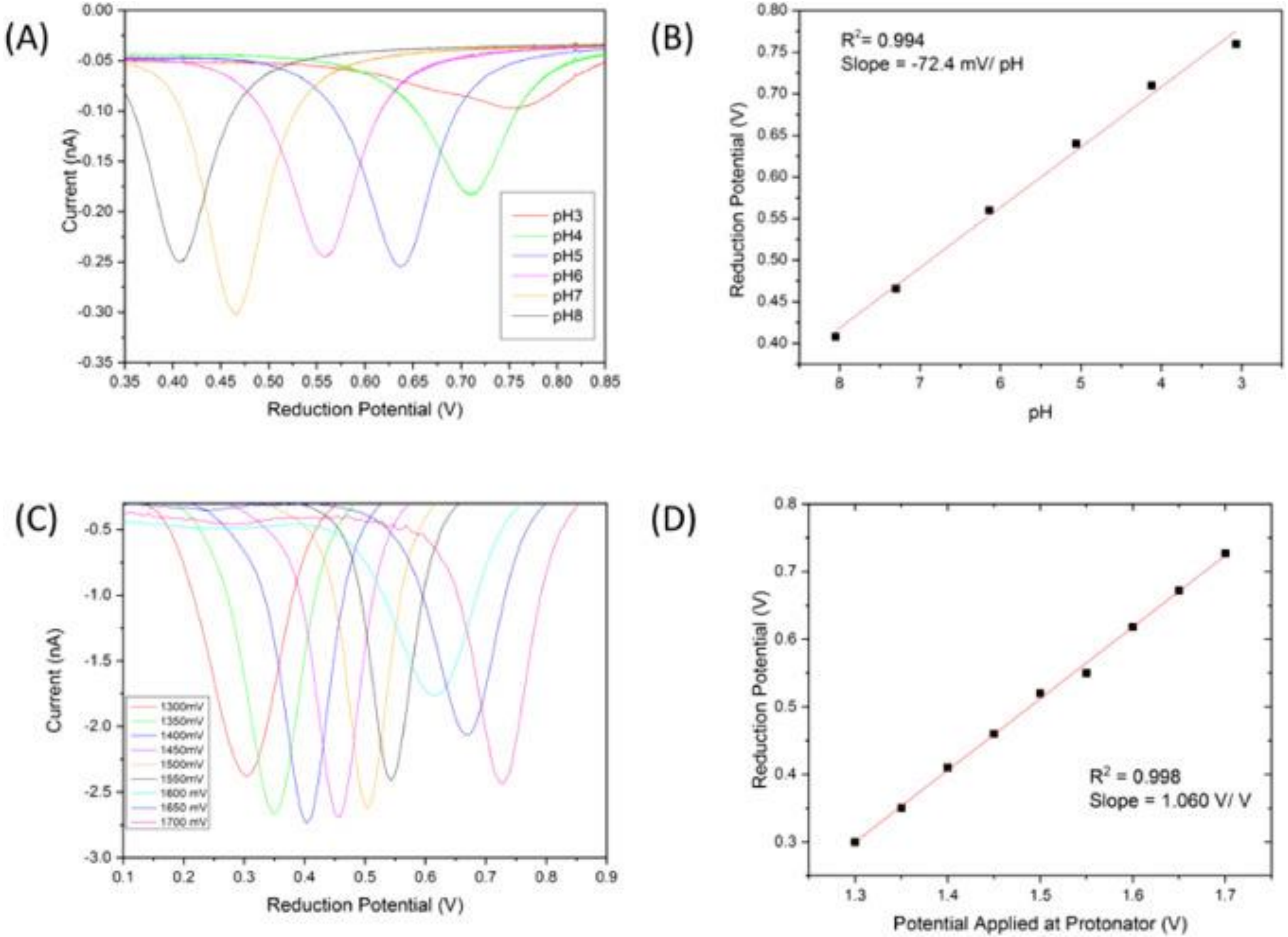


Visualisation of pH change using crystal violet pH indicator dye.

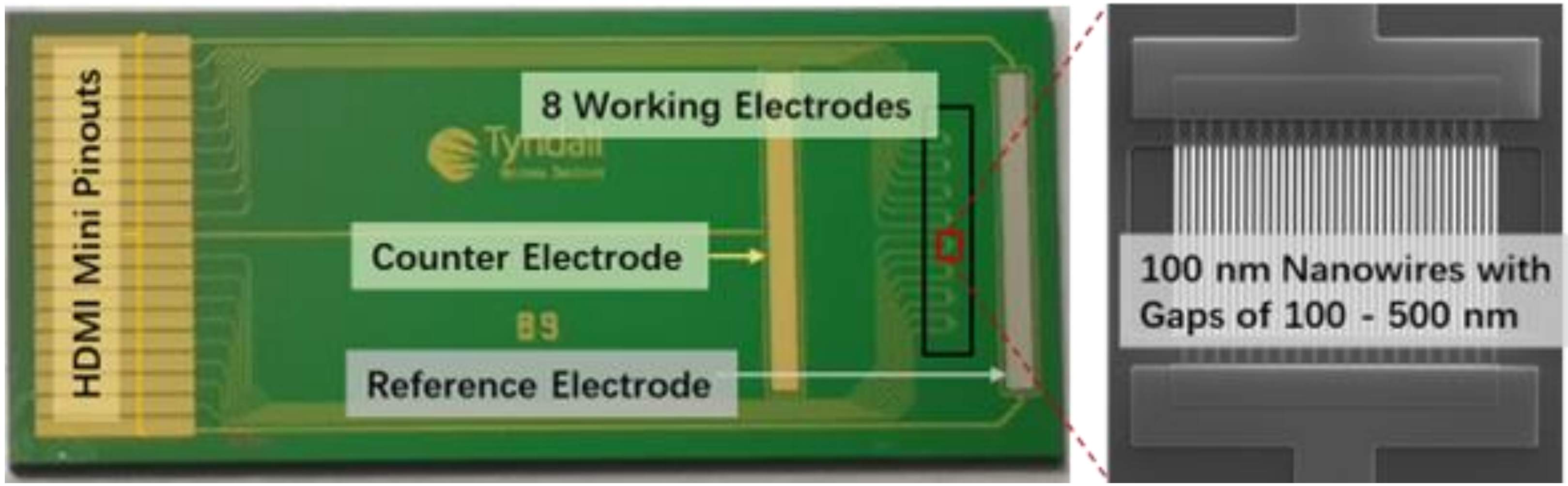
Oxidation: $2\ H_2O(l) \rightarrow O_2\ (g) + 4\ H^+(aq) + 4e^-$

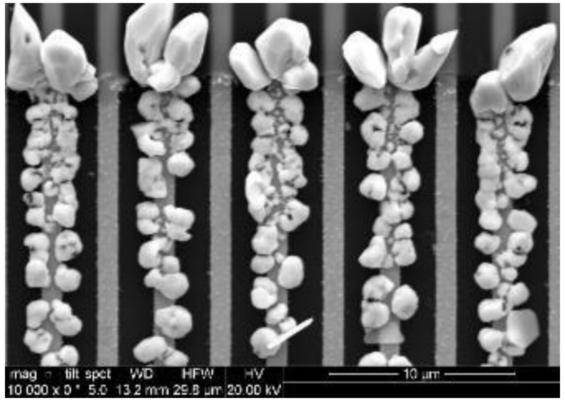
Reduction: $2\ H^+(aq) + 2e^- \rightarrow H_2\ (g)$

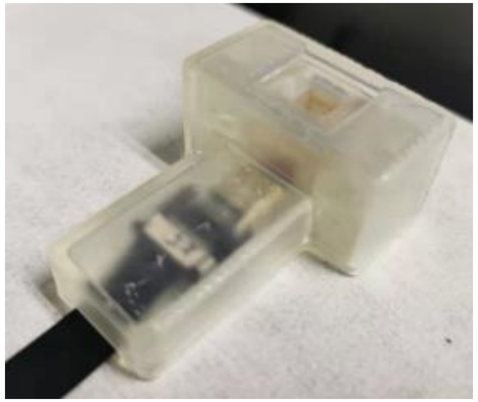
Electrochemical In-situ pH control

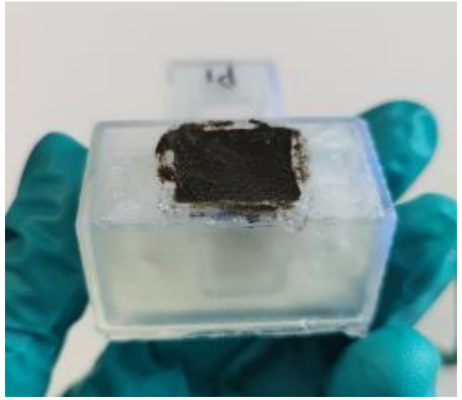


Nitrate detection: Materials Development (Selectivity)

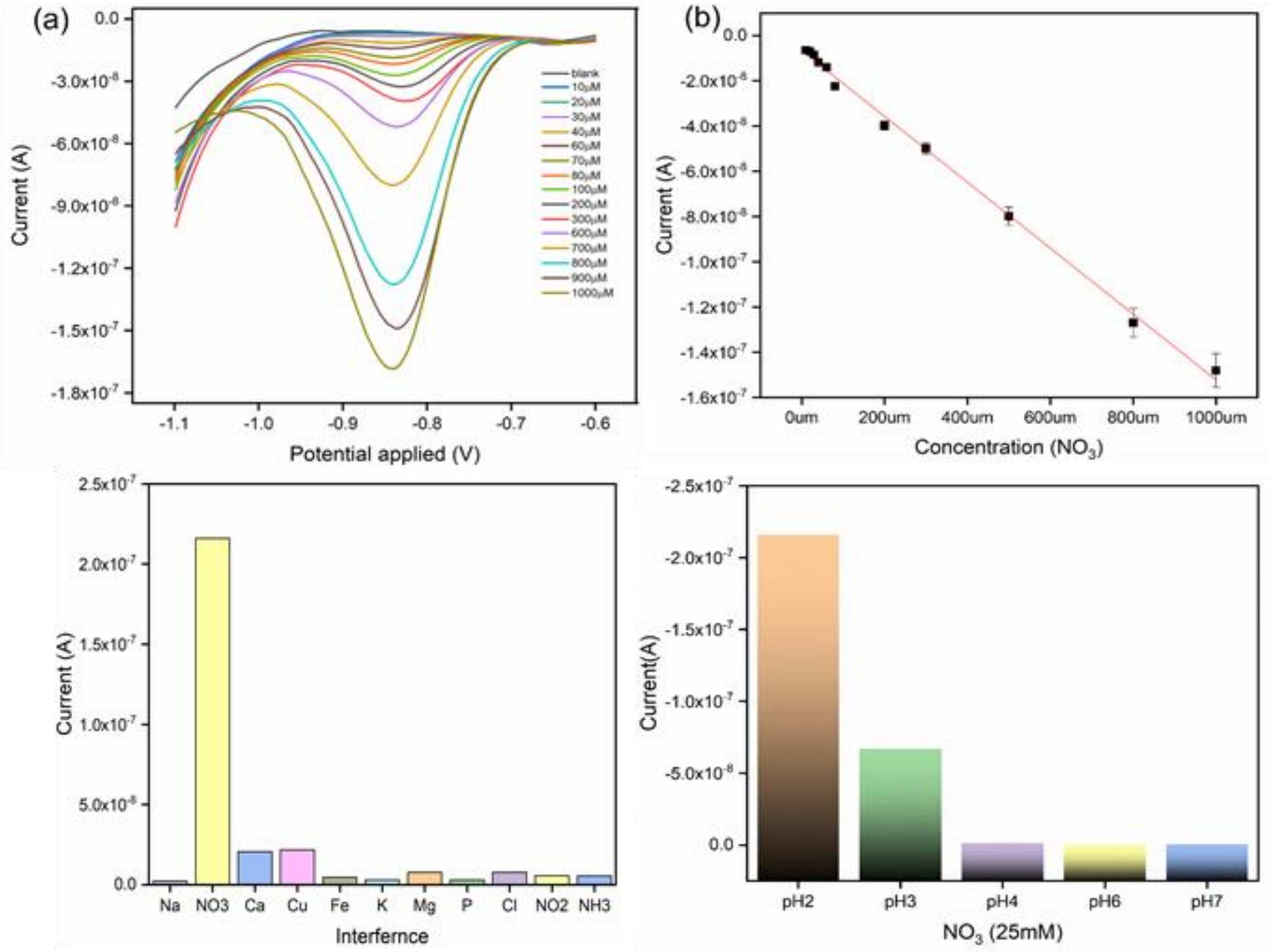


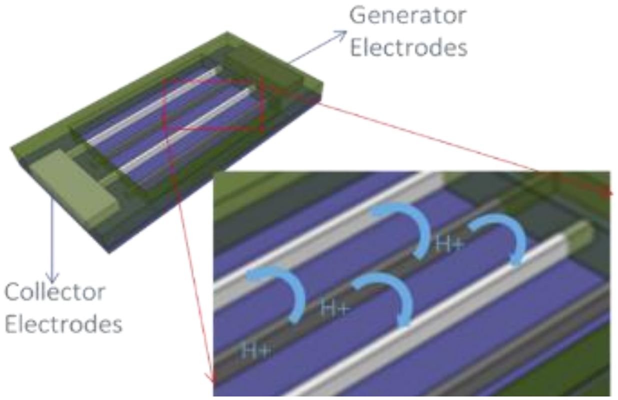


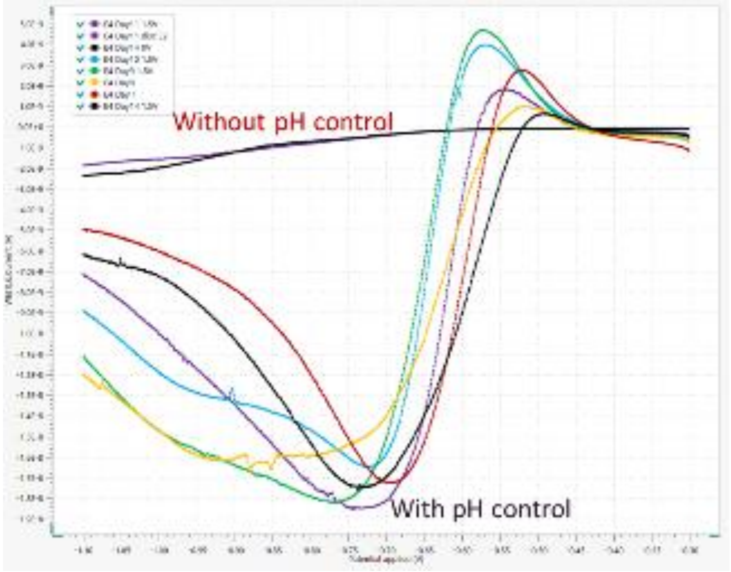




Nitrate: Real-Time, On-Farm

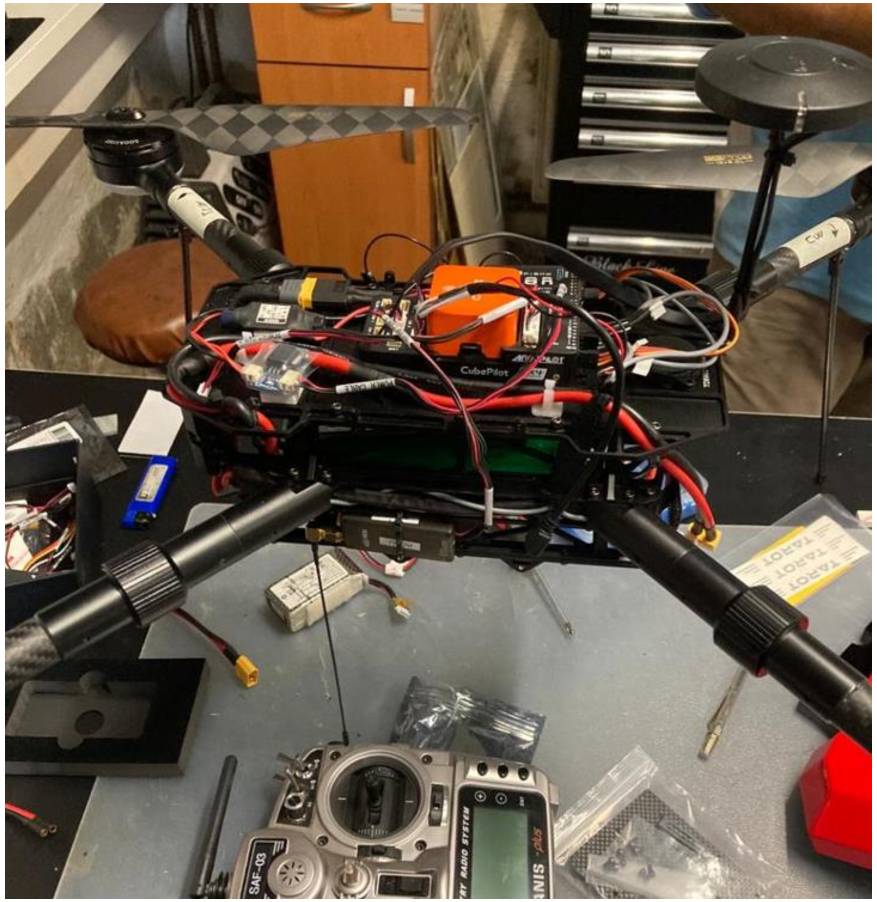






Local pH control

Preparation of field deployment

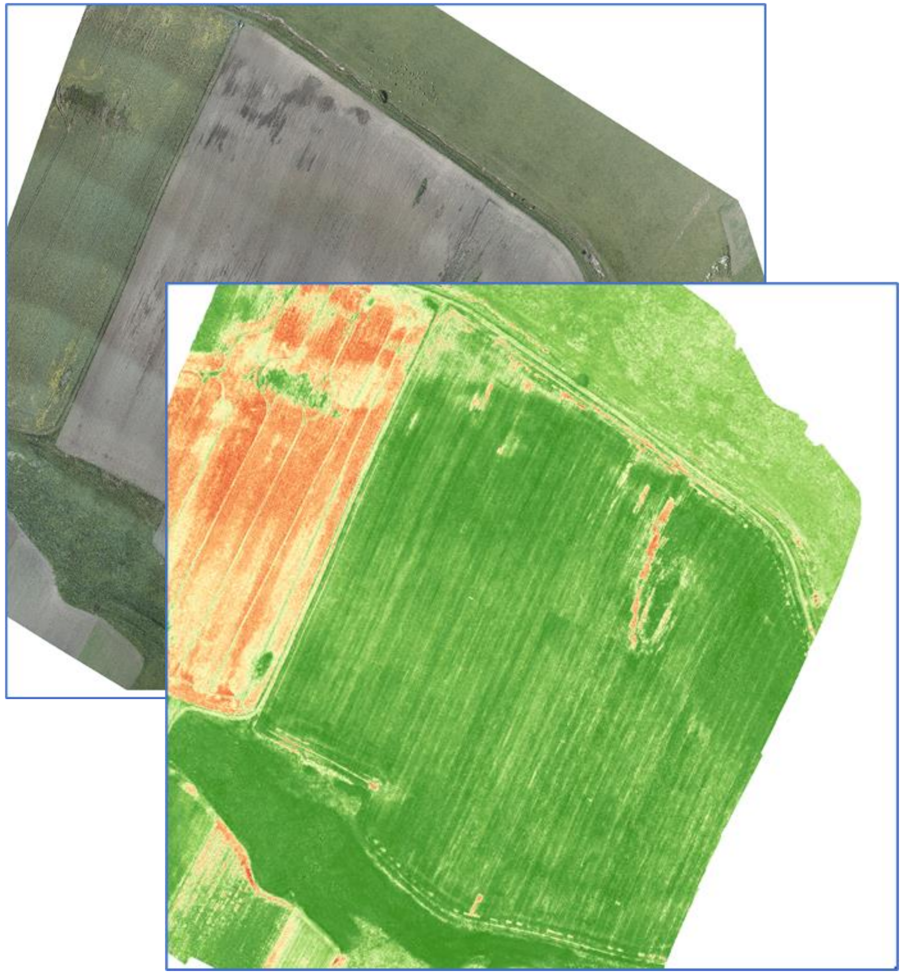


Gather historical map data

Validate flight infrastructure by :

- Performing flight tests with custom made quadcopter
- Integrate several cameras (ortho-photo, thermal and spectral – Micasense RedEdge MX) for best results

Preparation of field deployment



Validate collection and post process spectral data by:

- Using different flight scenarios
- Output data collected in a single format using software such as Pix4D and OpenDroneMap
- Post process spectral image (Tiff format) using QGis software for generating various spectral index maps (ENDVI, LAI, NDRE, NDVI)
- Compare output with SANTINEL satellite gather data

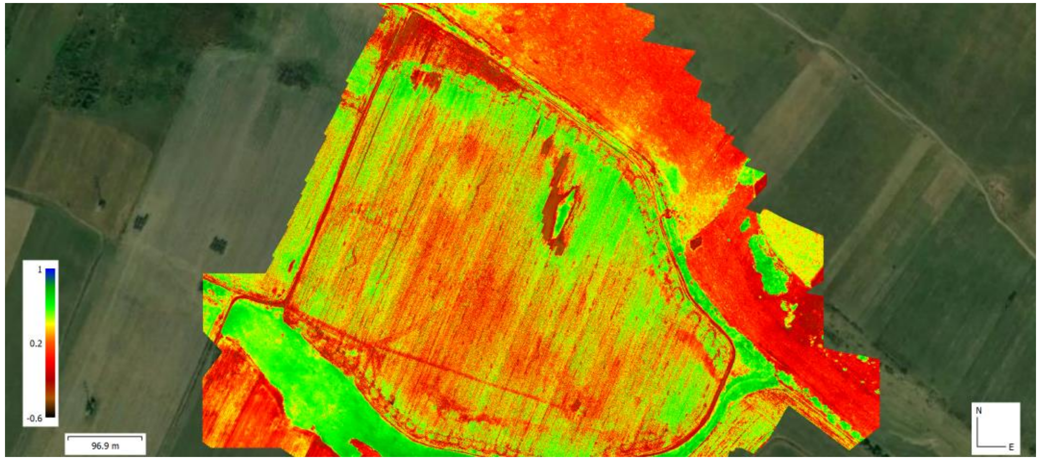
Sensor data validation and interpretation

Validation infrastructure setup

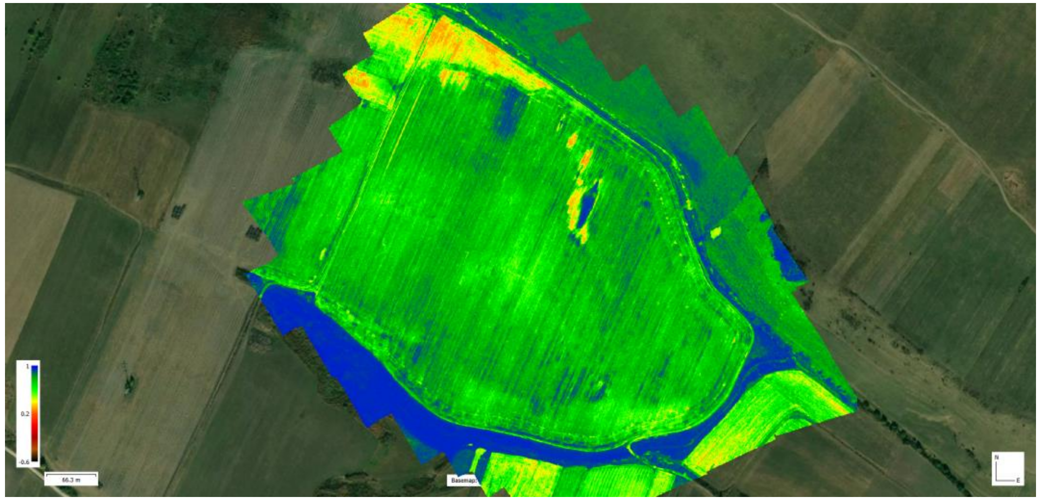
Continues spectral data collection from both satellite sources and drone mounted RedEdge Mx spectral camera

Data	Activitate/Fenofaza	Flight altitude (m)	Amount of data collected (GB)	Post-processing Tool
01-May	spectral imagery and ortho	50	14.30	DroneMap, Pix4D, Agisoft
15-May	spectral imagery and ortho	75	18.20	DroneMap, Pix4D, Agisoft
19-May	spectral imagery and ortho	50	26.90	Pix4D, Agisoft
09-Jun	spectral imagery and ortho	100	8.40	Agisoft, QGIS
16-Jun	ortho	100	2.82	Agisoft, QGIS
18-Jun	spectral imagery and ortho	100	11.10	Agisoft, QGIS
23-Jun	spectral imagery and ortho	100	10.50	Agisoft, QGIS
29-Jun	spectral imagery and ortho	100	10.00	Agisoft, QGIS
15-Jul	spectral imagery and ortho	100	11.60	Agisoft, QGIS
28-Jul	spectral imagery and ortho	100	7.70	Agisoft, QGIS
02-Aug	spectral imagery and ortho	100	8.06	Agisoft, QGIS
05-Aug	spectral imagery and ortho	100	15.60	Agisoft, QGIS
13-Aug	spectral imagery and ortho	100	8.56	Agisoft, QGIS
21-Aug	spectral imagery and ortho	100	8.18	Agisoft, QGIS
31-Aug	spectral imagery and ortho	100	8.30	Agisoft, QGIS
01-Oct	spectral imagery and ortho	100	8.06	Agisoft, QGIS
24-Oct	spectral imagery and ortho	100	8.23	Agisoft, QGIS

Tabel 1: Spectral imagery collection history

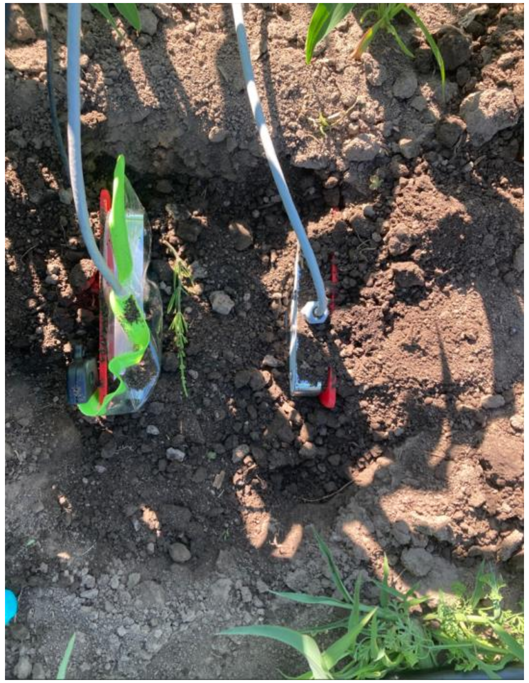


ENDVI spectral output 19.05.2022



NDVI spectral output 21.06.2022

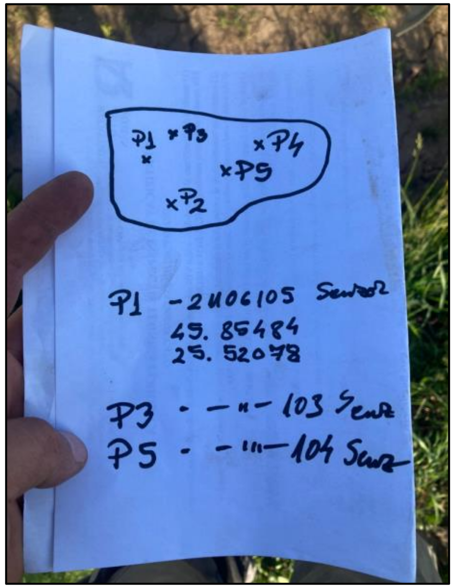
Sensor in field installation and maintenance

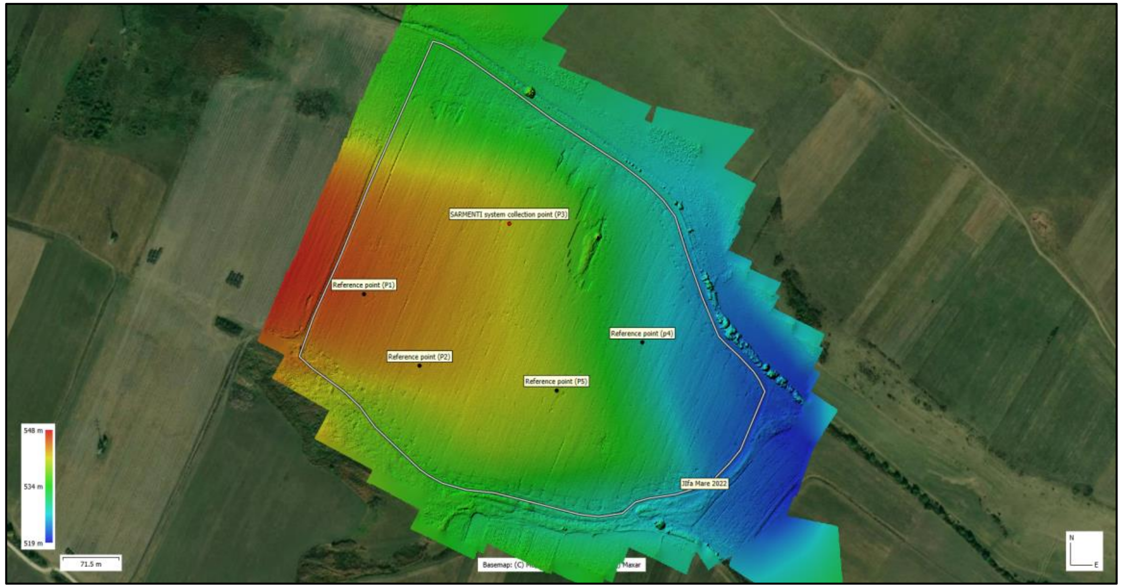


Reference soil sample collection

Aprox. every 10 days during crop life cycle, soil sample collection was performed from 5 different points of the field and classic lab analysis were performed

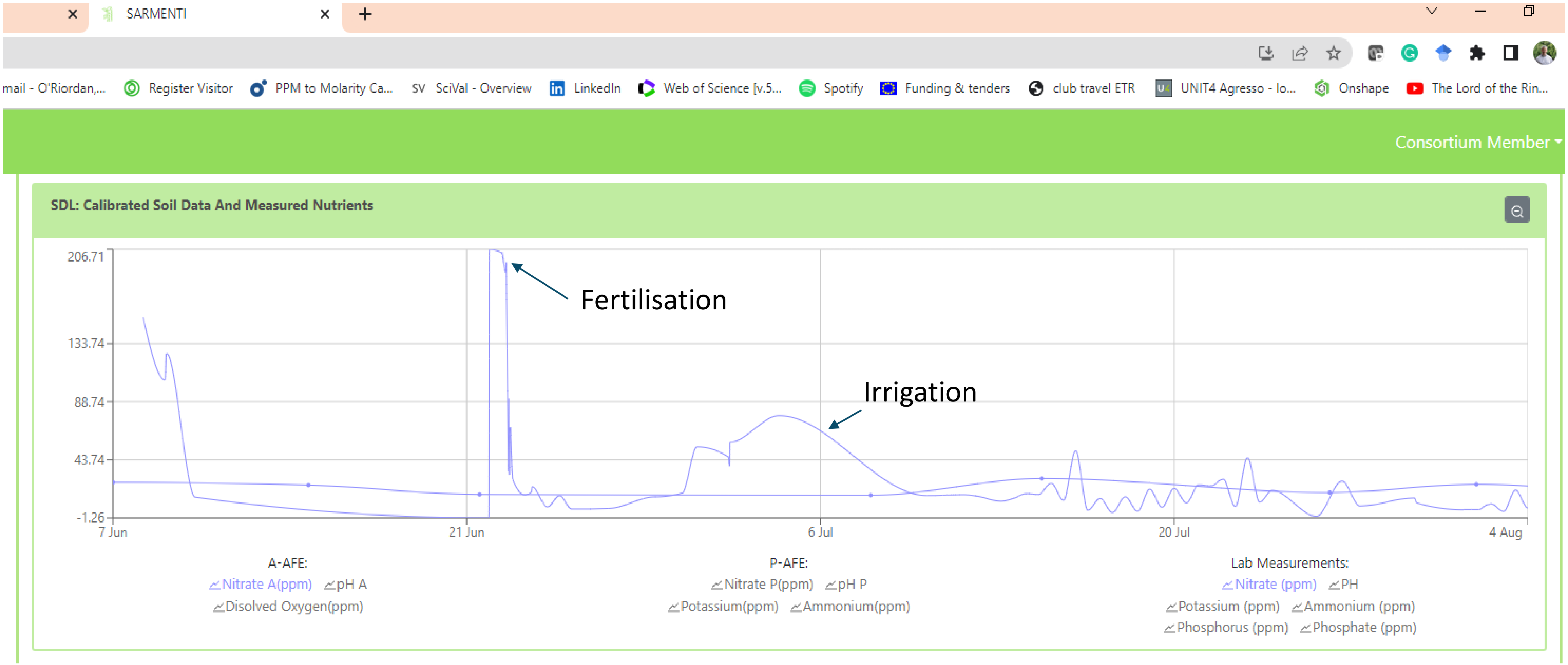
Results were inserted into Sarmenti Webpage, together with corn life cycle stages





In field reference points distribution

Back end server

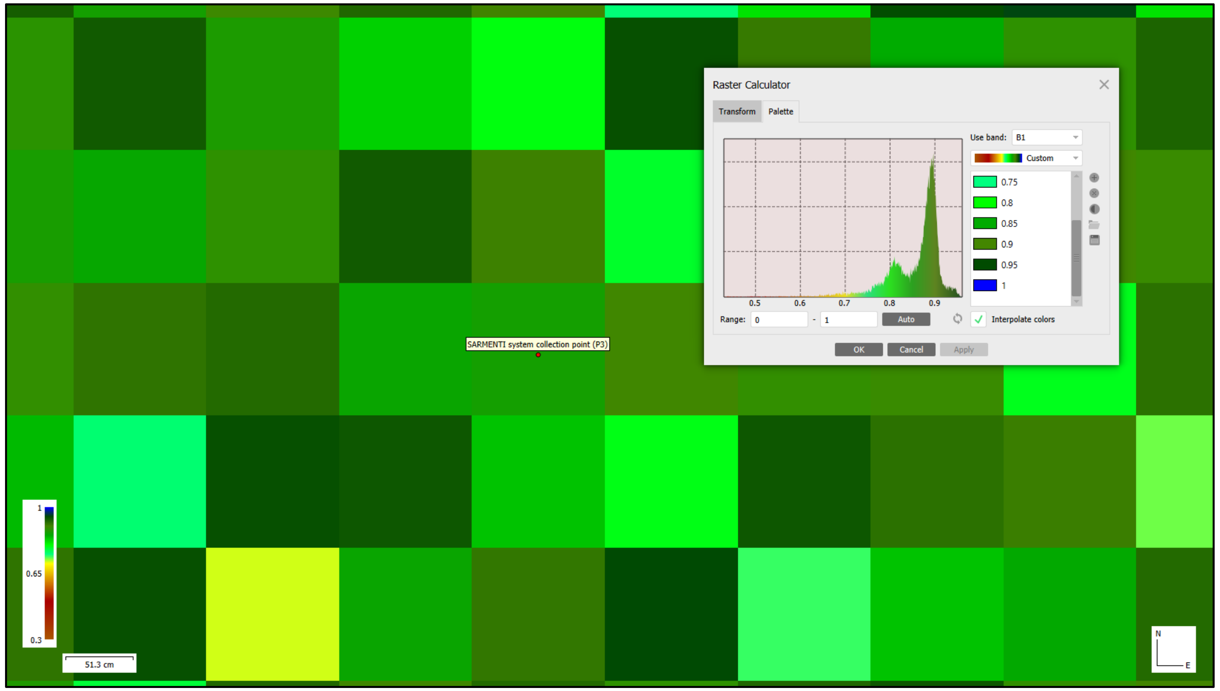


Sensor Fusion

Validation infrastructure setup

In vegetation fertilization decision based on nitrogen sensor readings and soil samples collection with urea prill on 22.06.2022, using variable spread rate

NDVI index map (1sqm/pixel resolution) (21.06.2022)



Detail of NDVI index value (0.887), corresponding to location where SARMENTI system was installed, collected on 21.06.2022 with Micasense RedEdge Mx spectral camera

This project has received funding from the European Union's Horizon 2020 Research and Innovation programme under grant agreement 825325

Sensor informed fertilisation strategy

Operationalize of Vicon RO-M Geospread 2008 fertilization machine GPS driven (20.05.2022), for applying in season granulate fertilizers such as urea with variable spread rate.

Urea spreading in-season with John Deere 6800 tractor and Vicon Geospread RO-M fertilizer machine driven and controlled with Trimble CFX GPS system

Achievements

Sarmenti system and its web application:

- All data produced by the Sarmenti project
- Can support the farmer with data presentation and decision making
- Allows viewing real-time evolution of field conditions
- Enables farmers to correlate weather events with nutrients evolution and plant response

From Spiro point of view:

- Agronomical practice is improved by using Sarmenti built tools
- Economical efficiency has improved (500 kg of less urea over 21 Ha)
- Environmental hazards (Nitrate losses) are reduced

System was functional up until 23rd of January 2023 (6+ months), including a few very harsh winter days ☺

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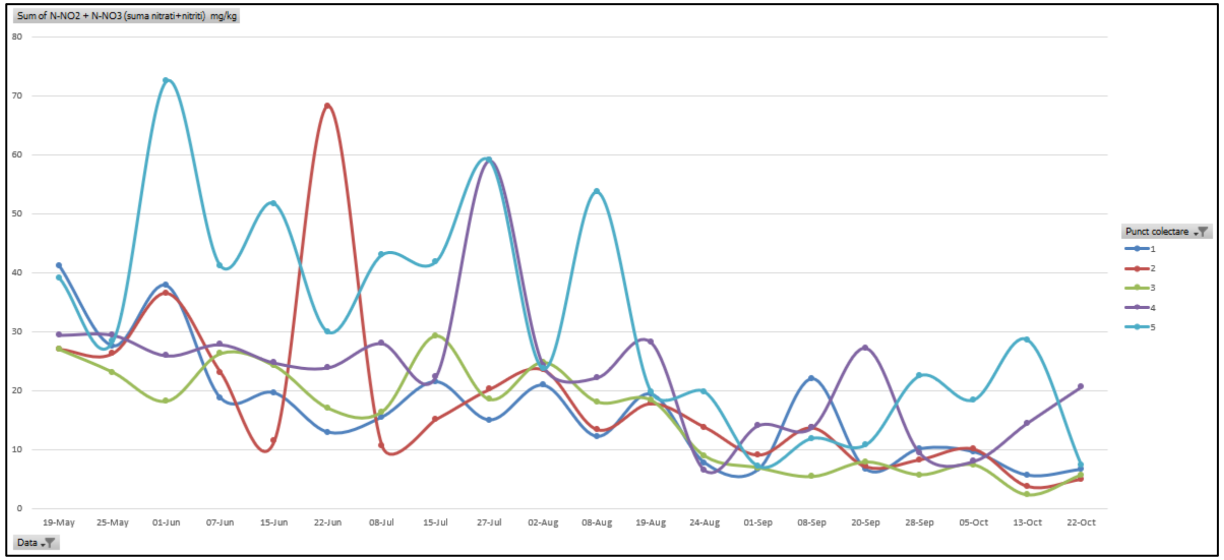
Reference soil sample collection

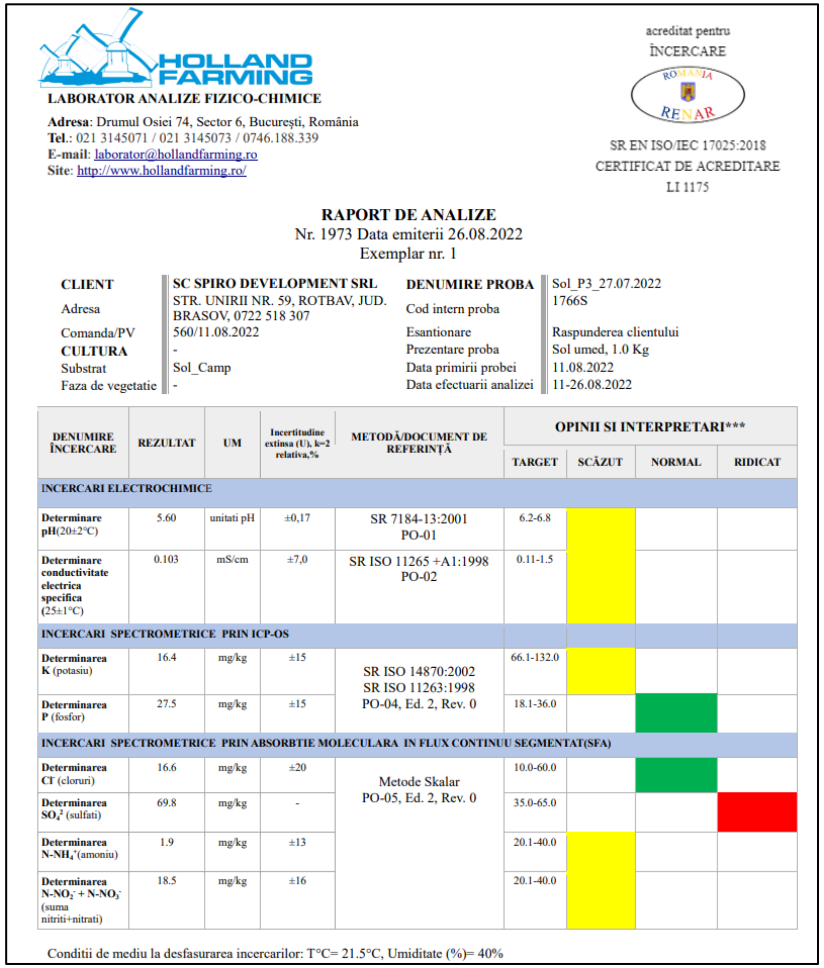
SPIR

Reference soil sample collection

A total of 96 soil samples were collected between seeding and harvesting (20 different dates for 5 different points) and 5 new ones collected exclusively for P3 (SARMENTI system reference point) after harvest, during November and beginning of December



Example of lab analysis result evolution for total amount of Nitrogen content



HOLLAND FARMING

LABORATOR ANALIZE FIZICO-CHIMICE

Adresa: Drumul Osiei 74, Sector 6, București, România
Tel.: 021 3145071 / 021 3145073 / 0746.188.339
E-mail: laborator@hollandfarming.ro
Site: http://www.hollandfarming.ro/

acreditat pentru
ÎNCERCARE
ROMANIA RENAR
SR EN ISO/IEC 17025:2018
CERTIFICAT DE ACREDITARE
LI 1175

RAPORT DE ANALIZE
Nr. 1973 Data emiterii 26.08.2022
Exemplar nr. 1

CLIENT	**SC SPIRO DEVELOPMENT SRL**	**DENUMIRE PROBA**	Sol_P3_27.07.2022
Adresa	STR. UNIRII NR. 59, ROTBAV, JUD. BRASOV, 0722 518 307	Cod intern proba	1766S
Comanda/PV	560/11.08.2022	Esantionare	Raspunderea clientului
CULTURA	-	Prezentare proba	Sol umed, 1.0 Kg
Substrat	Sol_Camp	Data primirii probei	11.08.2022
Faza de vegetatie	-	Data efectuarii analizei	11-26.08.2022

DENUMIRE ÎNCERCARE	REZULTAT	UM	Incertitudine extinsa (U), k=2 relativa,%	METODĂ/DOCUMENT DE REFERINȚĂ	OPINII SI INTERPRETARI***			
					TARGET	SCĂZUT	NORMAL	RIDICAT
INCERCARI ELECTROCHIMICE								
Determinare pH(20±2°C)	5.60	unitati pH	±0,17	SR 7184-13:2001 PO-01	6.2-6.8			
Determinare conductivitate electrica specifica (25±1°C)	0.103	mS/cm	±7,0	SR ISO 11265 +A1:1998 PO-02	0.11-1.5			
INCERCARI SPECTROMETRICE PRIN ICP-OS								
Determinarea K (potasiu)	16.4	mg/kg	±15	SR ISO 14870:2002 SR ISO 11263:1998 PO-04, Ed. 2, Rev. 0	66.1-132.0			
Determinarea P (fosfor)	27.5	mg/kg	±15		18.1-36.0			
INCERCARI SPECTROMETRICE PRIN ABSORBTIE MOLECULARA IN FLUX CONTINUU SEGMENTAT(SFA)								
Determinarea Cl^- (cloruri)	16.6	mg/kg	±20	Metode Skalar PO-05, Ed. 2, Rev. 0	10.0-60.0			
Determinarea SO_4^{2} (sulfati)	69.8	mg/kg	-		35.0-65.0			
Determinarea $N\text{-}NH_4^+$(amoniu)	1.9	mg/kg	±13		20.1-40.0			
Determinarea $N\text{-}NO_2^- + N\text{-}NO_3^-$ (suma nitriti+nitrati)	18.5	mg/kg	±16		20.1-40.0			

Conditii de mediu la desfasurarea incercarilor: T°C= 21.5°C, Umiditate (%)= 40%

Example of analyse report for soil sample P3 collected on 27.07.2022

Residual Chlorine: pH Control

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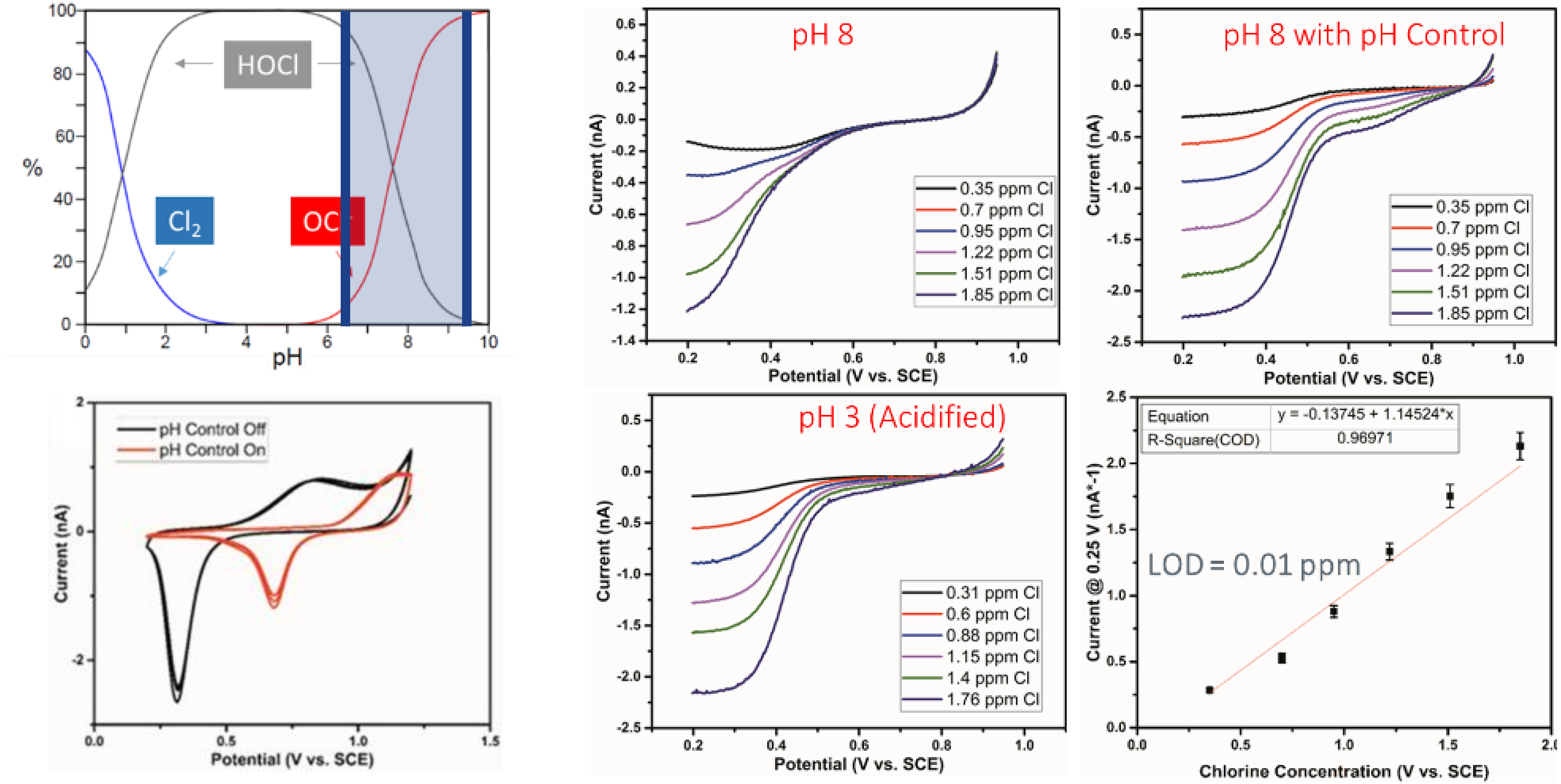

2020. Sensors and Actuators B: Chemical, DOI: 10.1016/j.snb.2020.128774

Monochloramine: Eliminate O_2

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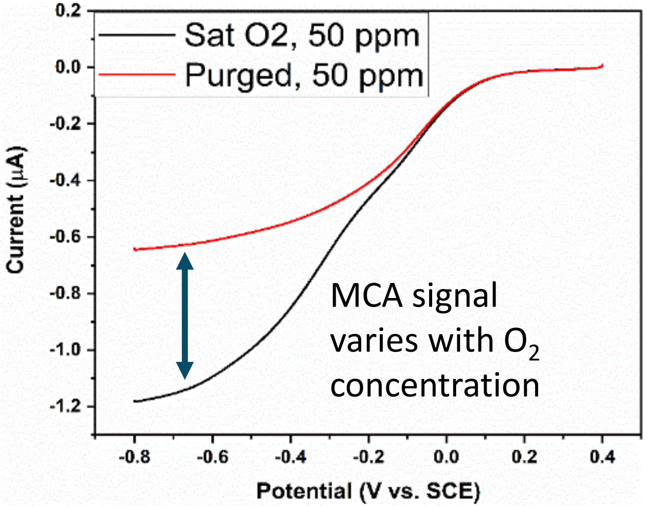
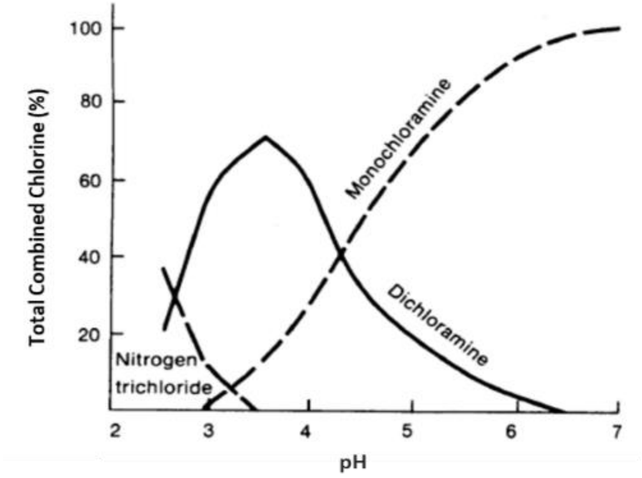
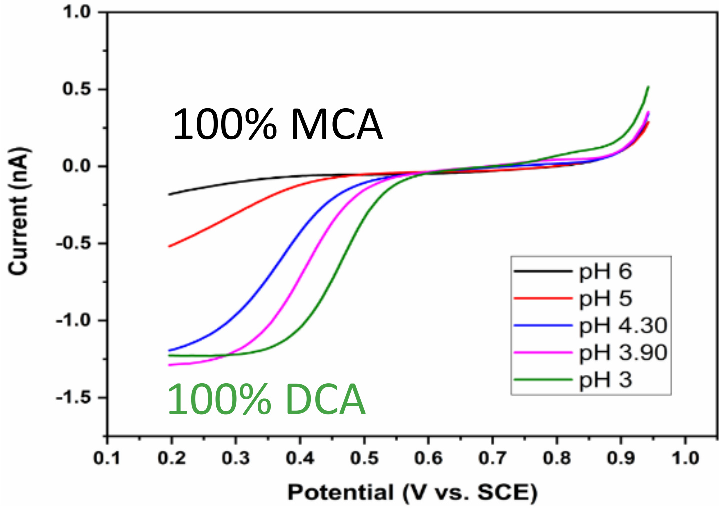
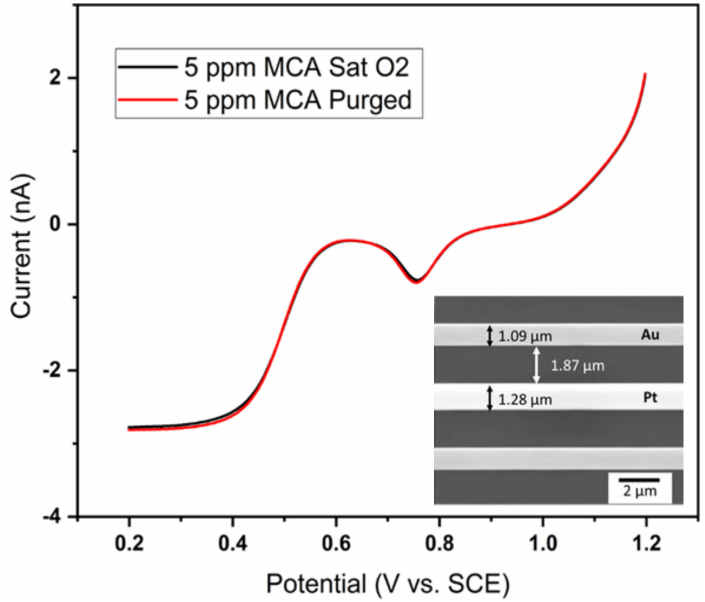
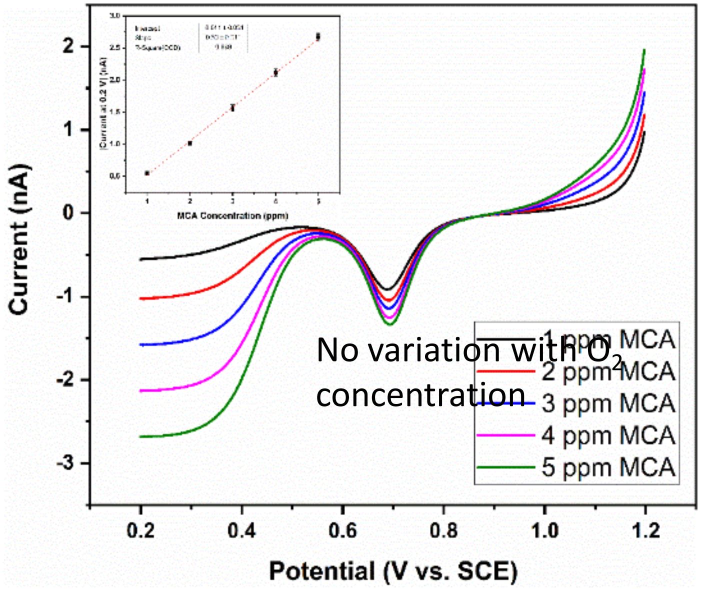
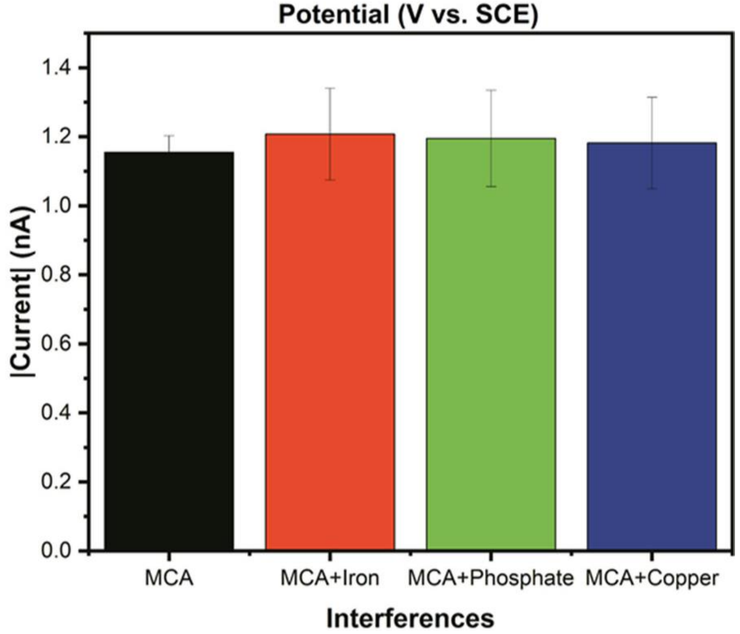






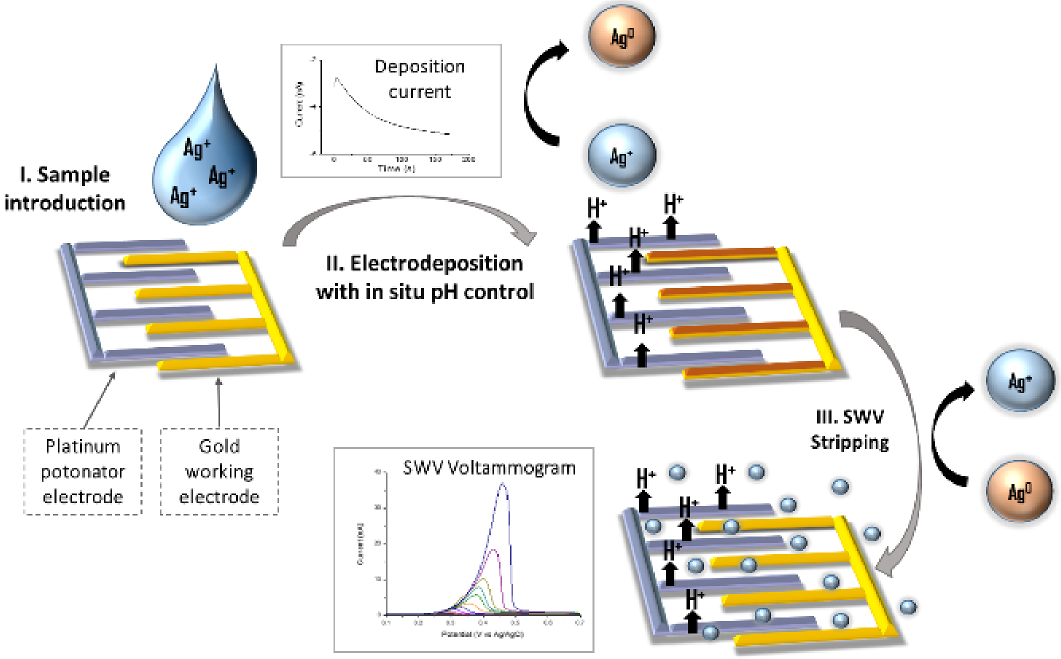


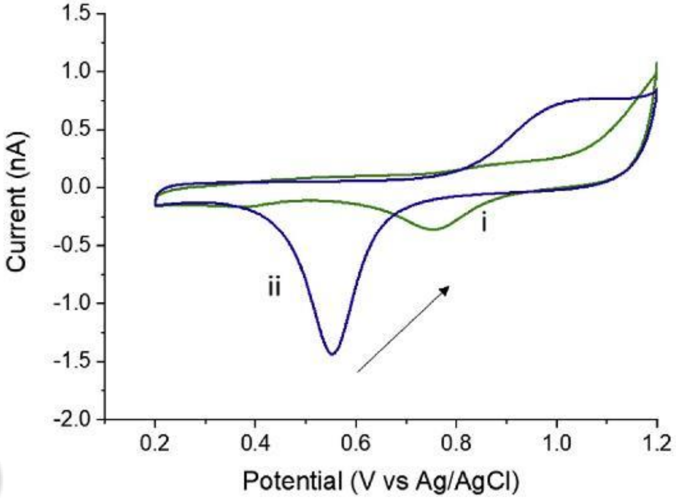


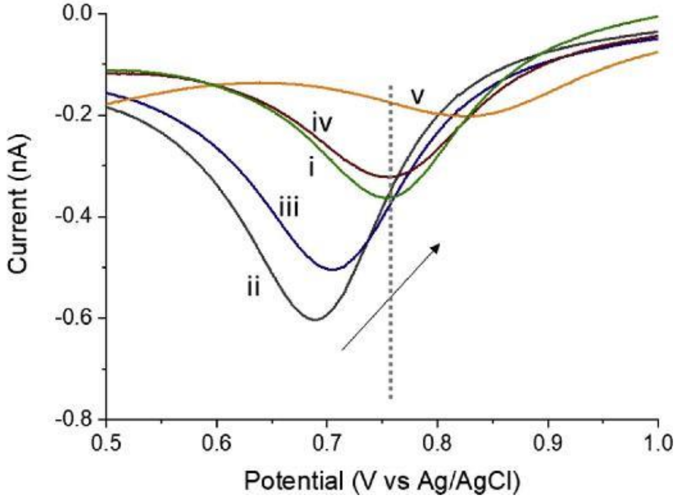


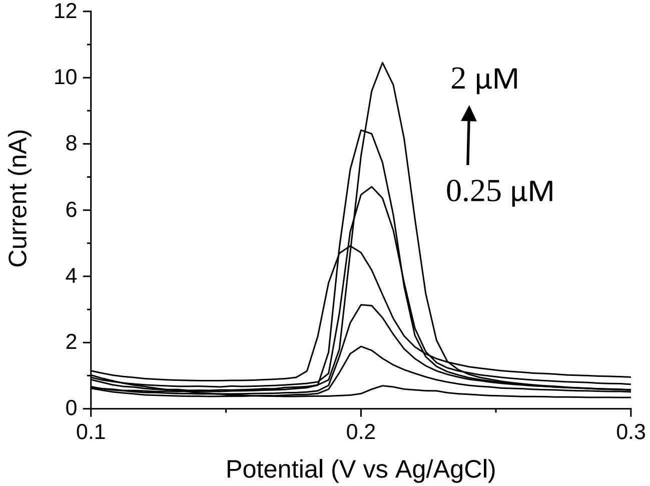
2021. ACS Sensors, DOI: 10.1021/acssensors.0c02264

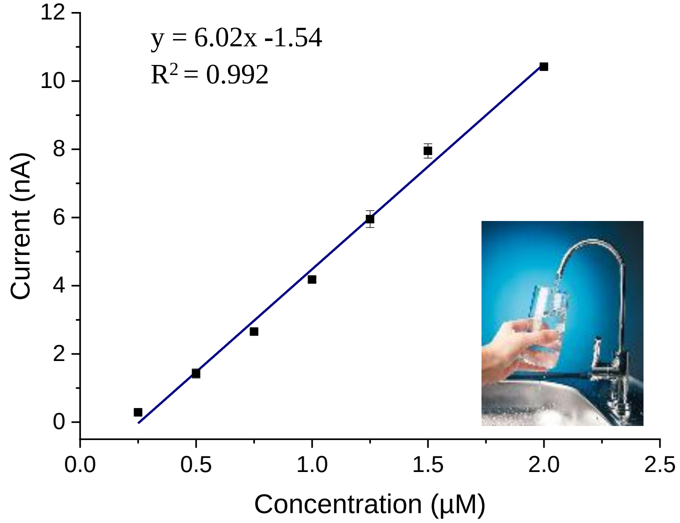
Silver: pH Control





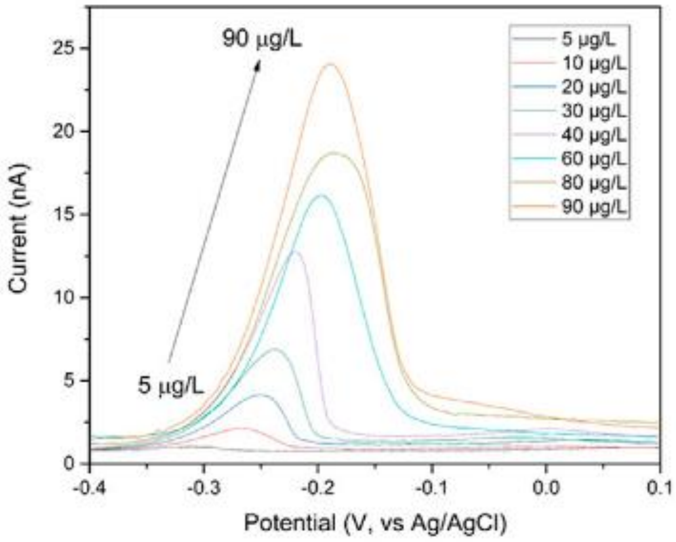




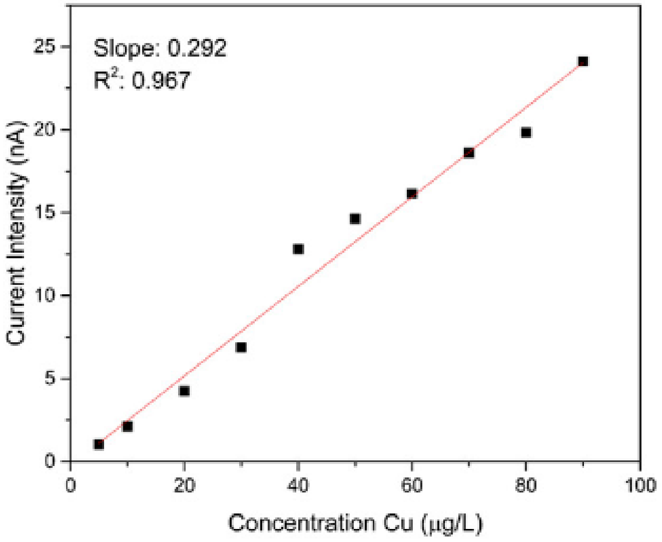


2021. Sensors and Actuators B: Chemical, DOI: .1016/j.snb.2021.129531

Copper: *In-situ* pH control



Sites	ICP-MS (µg/L)	Pt IDA Sensor (µg/L)
Avoca	22	17
Ross Mines	27	20
Bunmahon	<3	1



2021. Sensors, DOI: 10.3390/s21103544

Multiple metals: *In-situ* pH control

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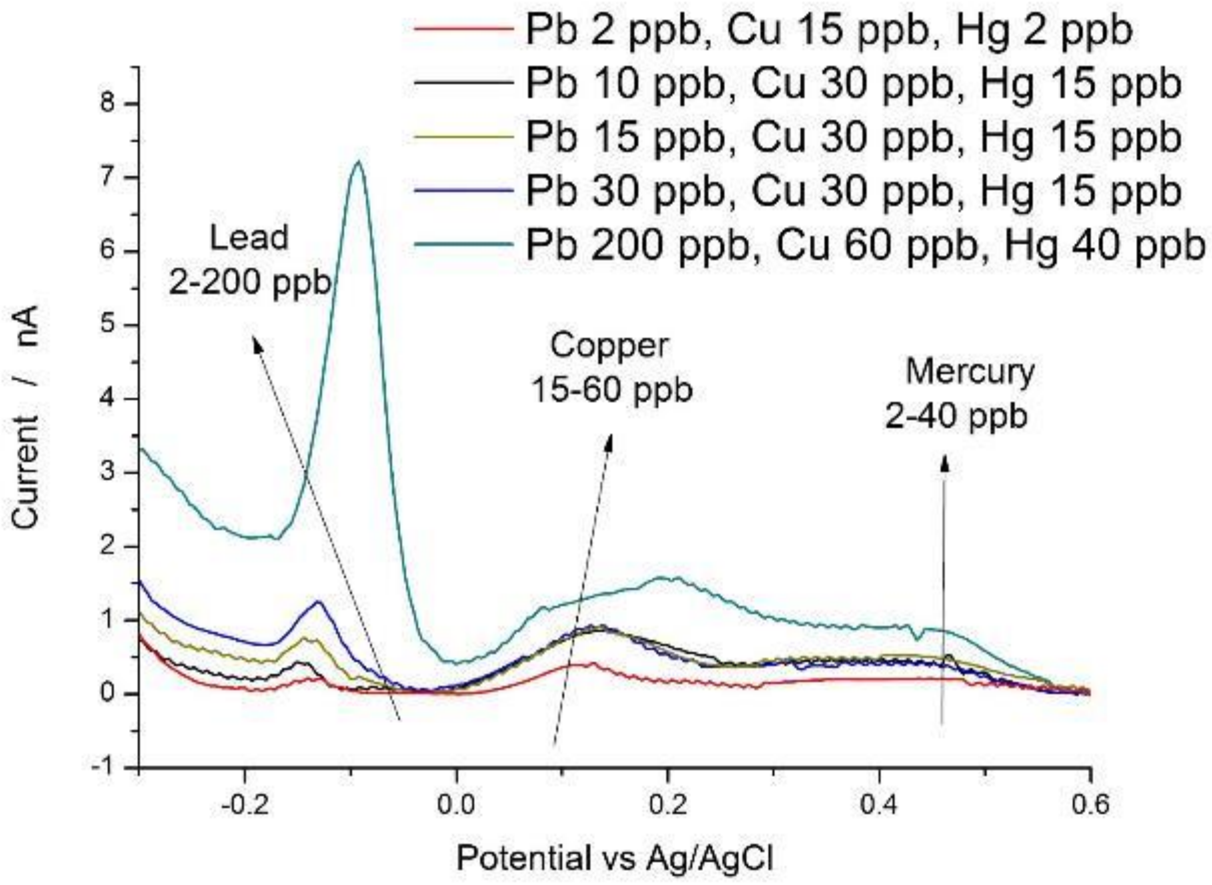

2023. Electrochimica Acta, DOI: 10.1016/j.electacta.2022.141668

Dissolved Oxygen: Interference-Free

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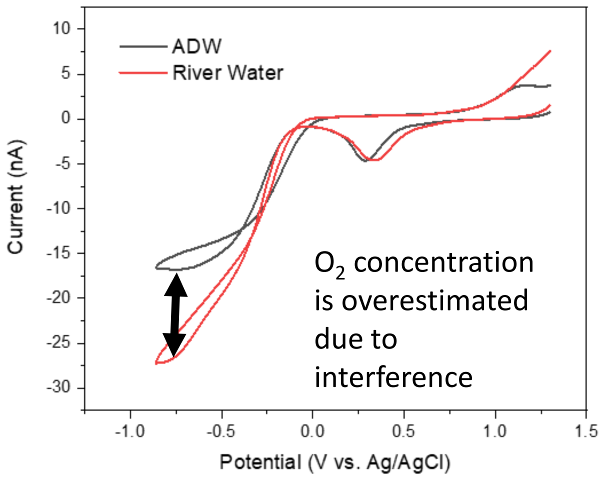
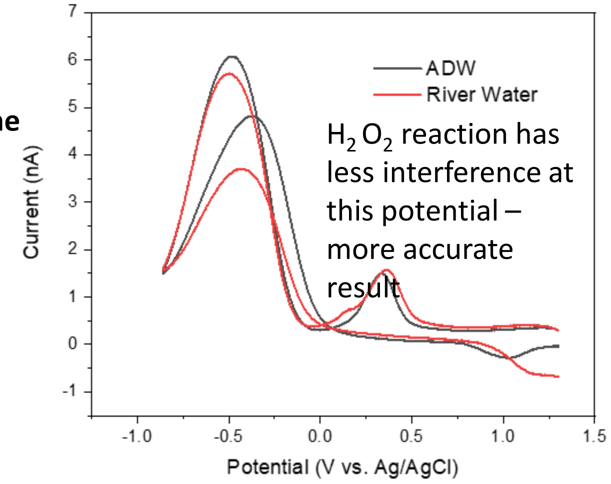
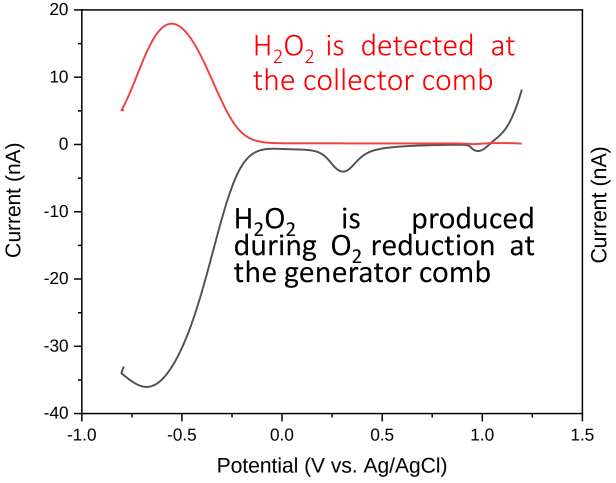
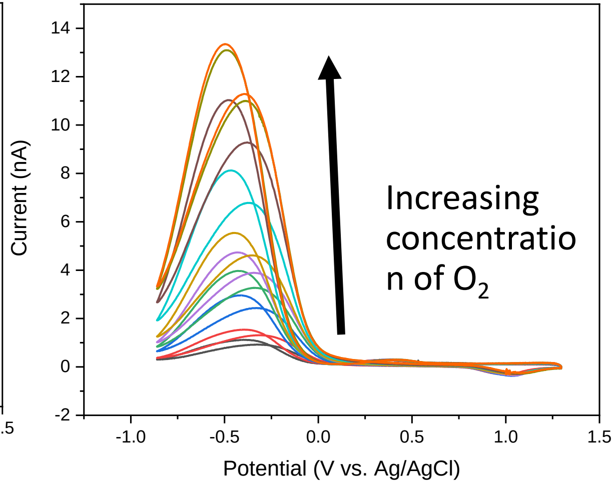


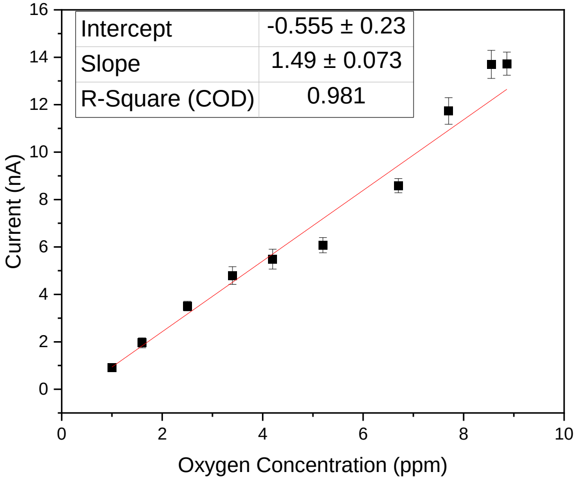
Non- GC Without Membrane

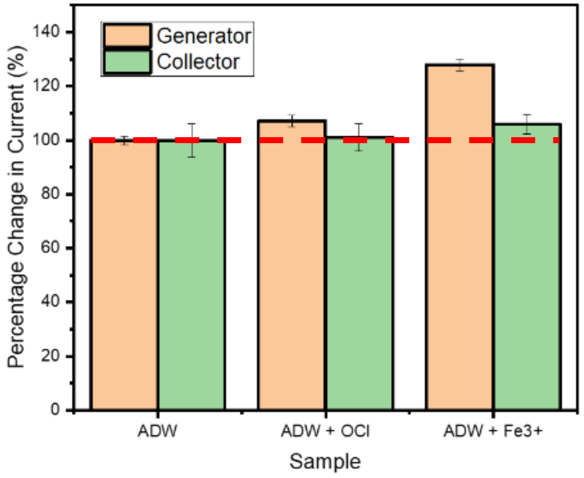
GC Without Membrane



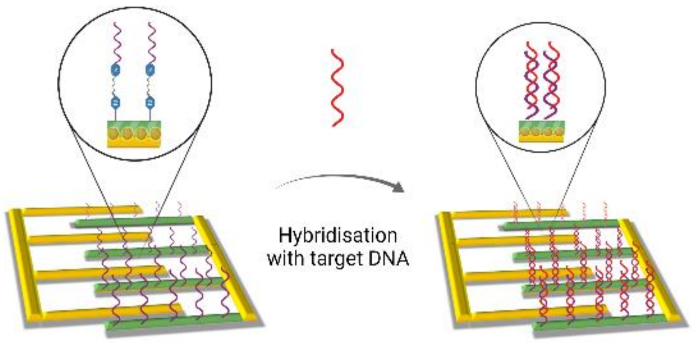


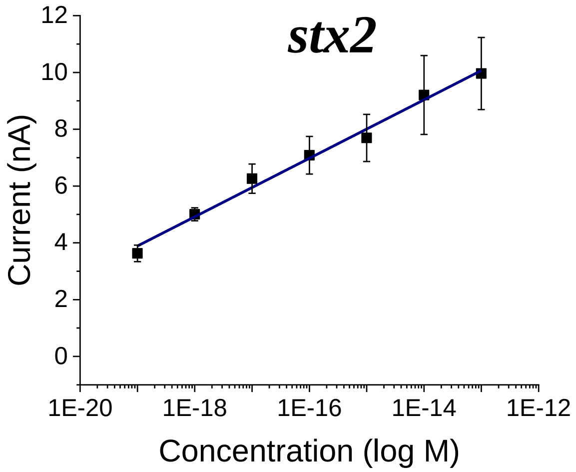


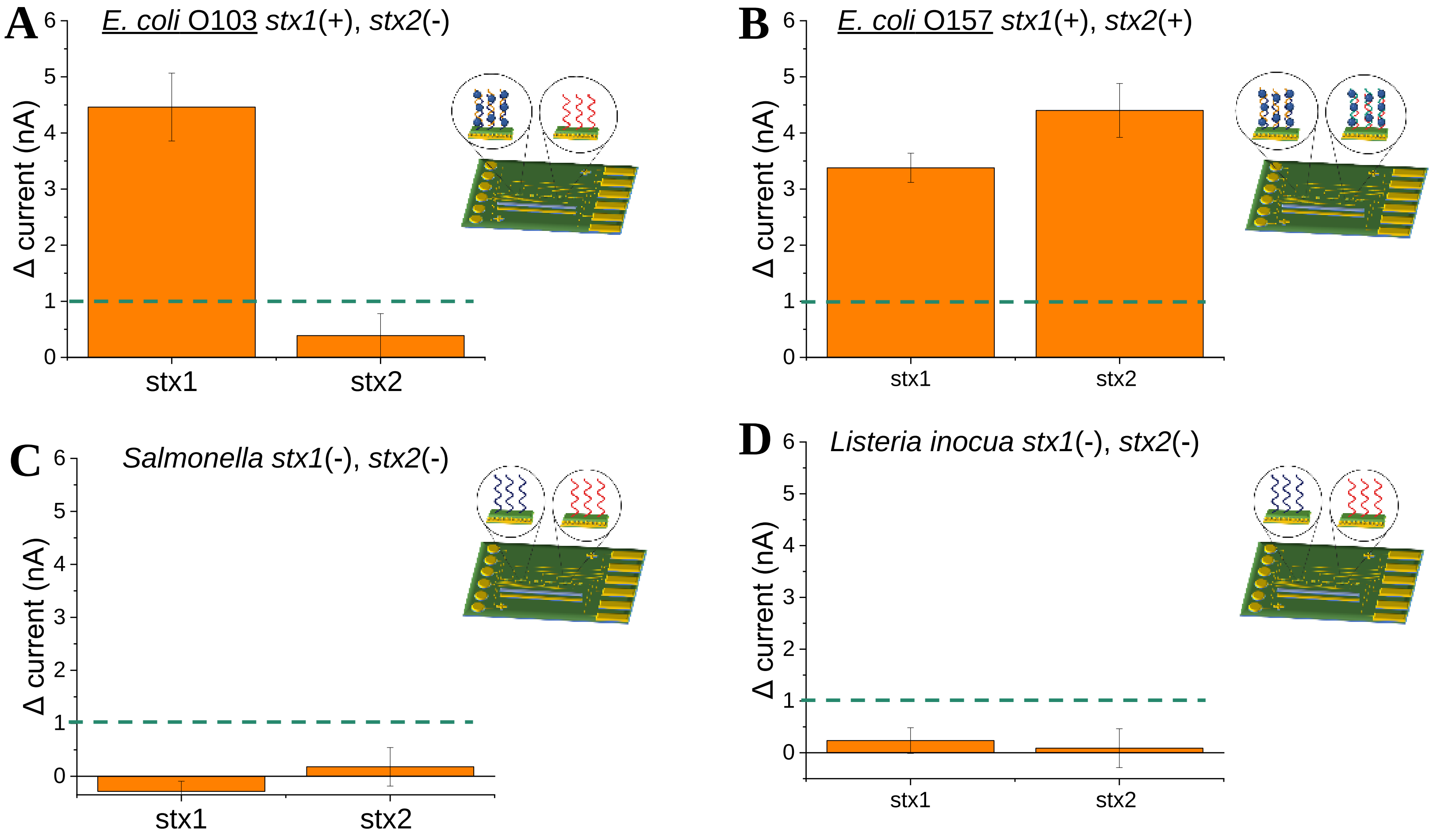




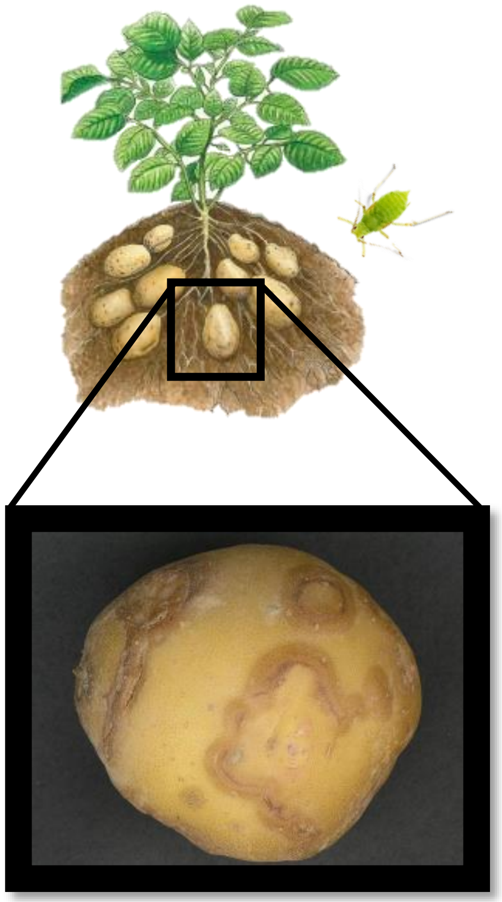
DNA-based E. *coli*



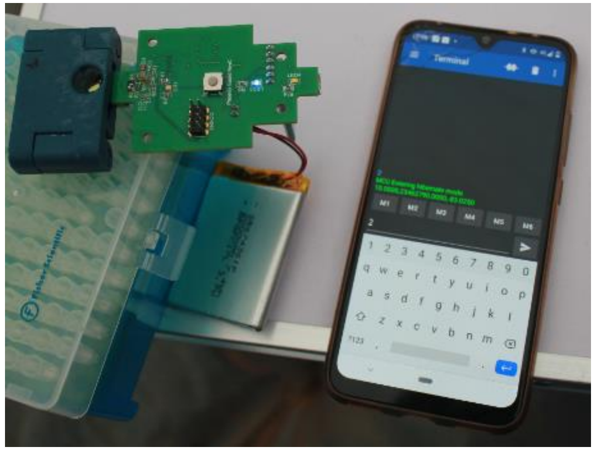


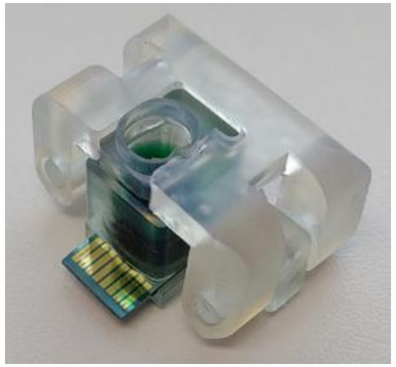


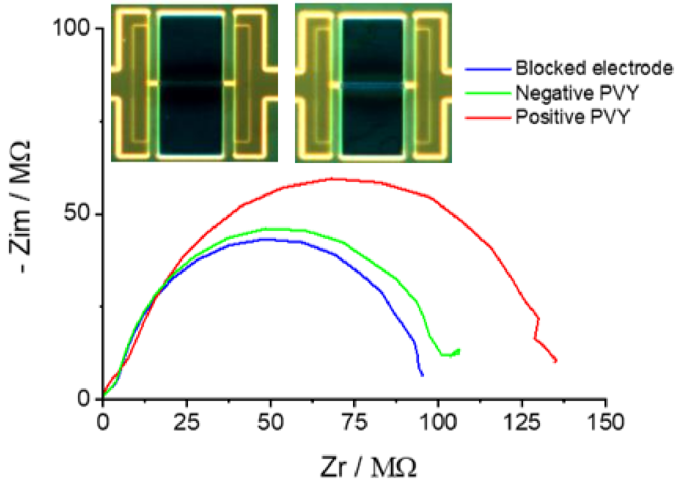
Virus: Real-Time, In-Field



Minimum Viable Product







Positive **Negative**

Virus: Benchmarking

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SAMPLE		ELISA (Absorbance)			PCR		Impedance (MΩ)	
ID	Variety	PVY	PVS	PVA	PVY	Ct RT-PCR	rRct (MΩ)	PVY Presence
155A	T8247/04	0,326 (P)	0,231(P)	0,2 (N)	P	14,515	32	LP
155B	T8247/04	0,114 (N)	1,72 (P)	0,189 (N)	N	29,505	27	N
156A	T8304/08	1,232 (P)	0,125 (N)	0,154 (N)	P	14,875	70	MP
156B	T8304/08	0,114 (N)	1,817 (P)	0,303 (P)	N	30,715	23	N
157A	T8310/03	1,897 (P)	0,191 (N)	0,144 (N)	P	14,755	100	MHP
160A	T8472/05	0,102 (N)	0,141 (N)	0,415 (P)	N	29,42	25	N
161B	T8486/02	2,538 (P)	0,108 (N)	0,2 (N)	P	14,505	250	HP
161A	T8486/02	0,232 (P)	0,19 (N)	0,208 (N)	P	15,63	35	LP
164A	T8560/07	0,977 (P)	0,111 (N)	0,166 (N)	P	14,995	57	MLP
165A	T8561/01	1,593 (P)	0,262 (P)	0,312 (P)	P	13,895	77	MP
166A	T8597/02	0,101 (N)	0,146 (N)	0,133 (N)	N	30,95	20	N

Abbreviations: P (Positive), N (Negative); LP (Low Positive) , MLP (Medium-low Positive); MP (Medium positive), MHP (Medium-High Positive); HP (High Positive); PVY (Potyvirus Y) PVS (Potyvirus S); PVA (Potyvirus A) Ct-PCR (cycle threshold PCR), Rct (Charge transfer resistance)

Nano-IDE Generator: Collector 2.0

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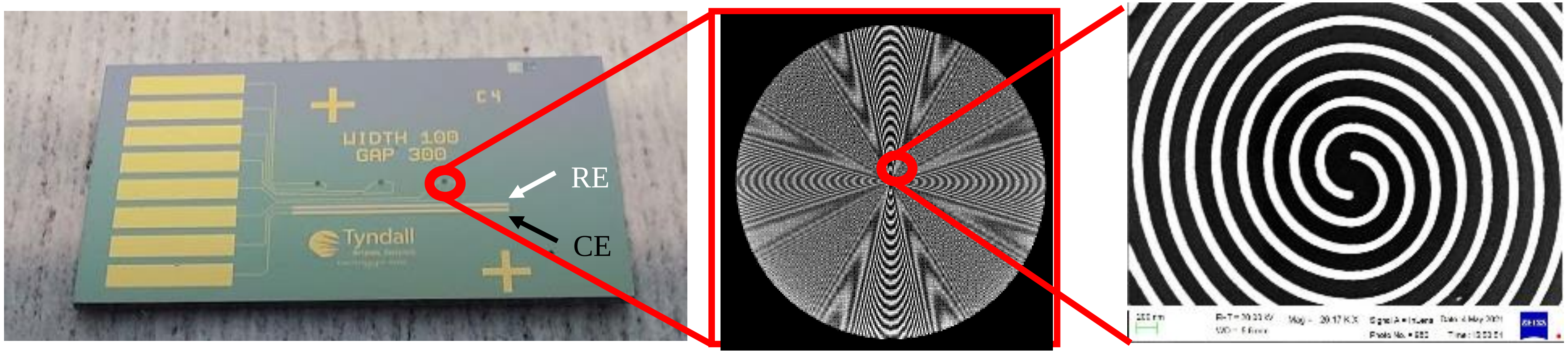
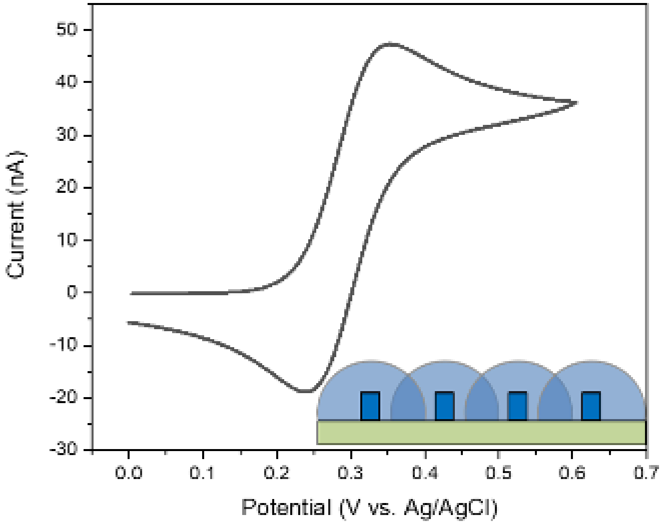
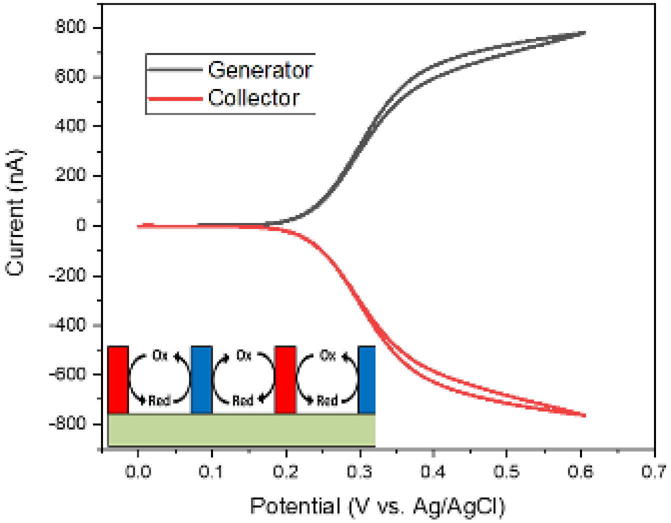


Non-GC Mode

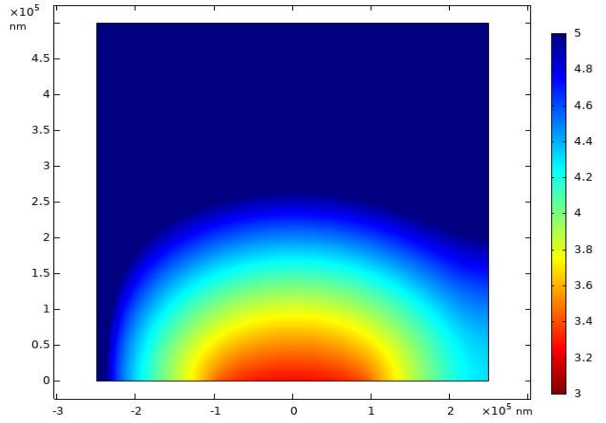


GC Mode

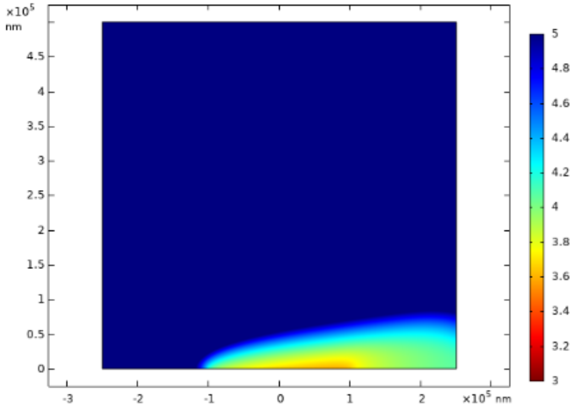


Work in progress.

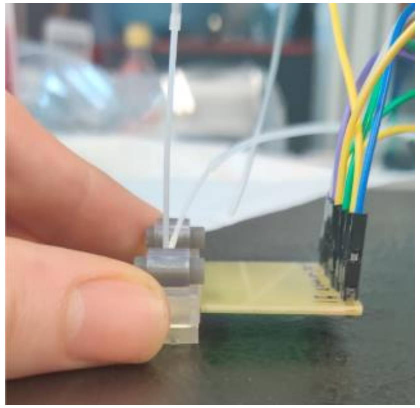
Micro-Fluidics



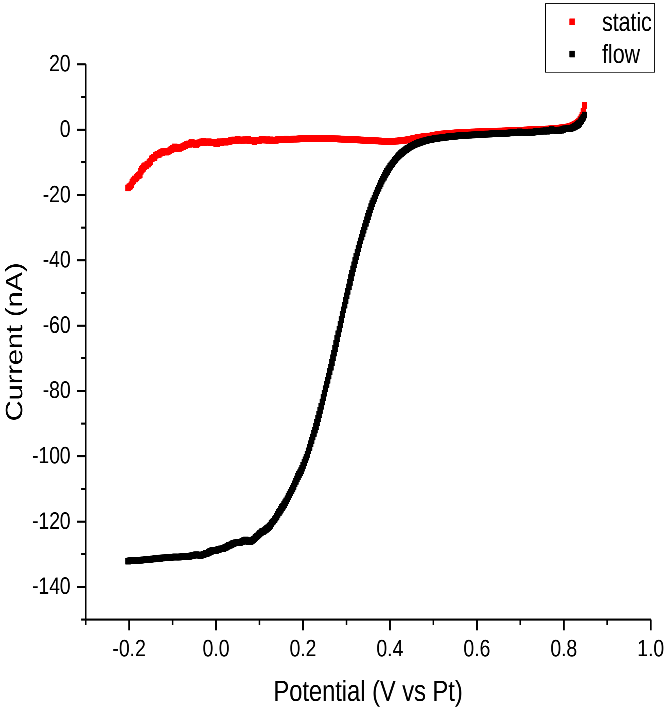
Static concentration profile



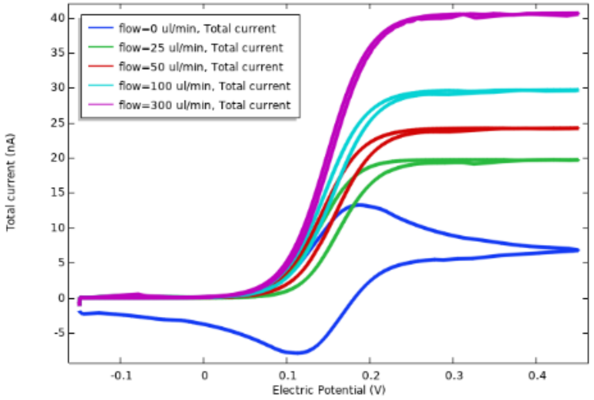
100 uL/min concentration profile



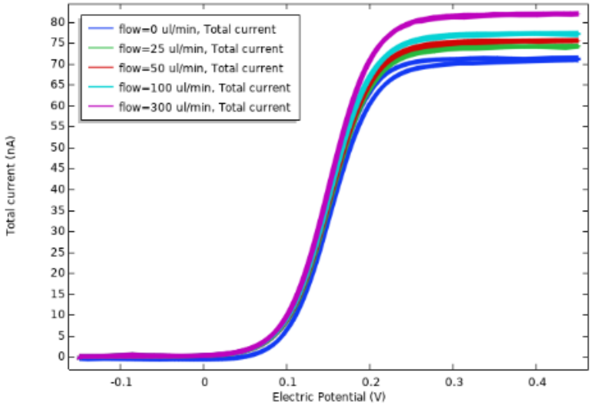
Assembled Microfluidics System



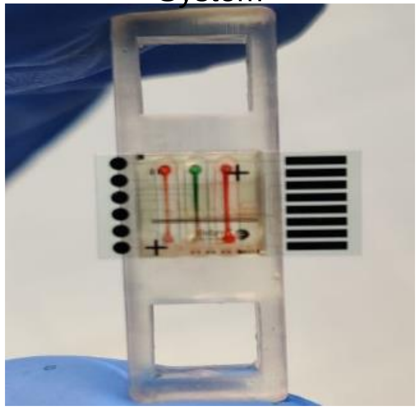
5.3ppm Chlorine detection in buffer with localised pH control



Simulation of effect of flow non CG

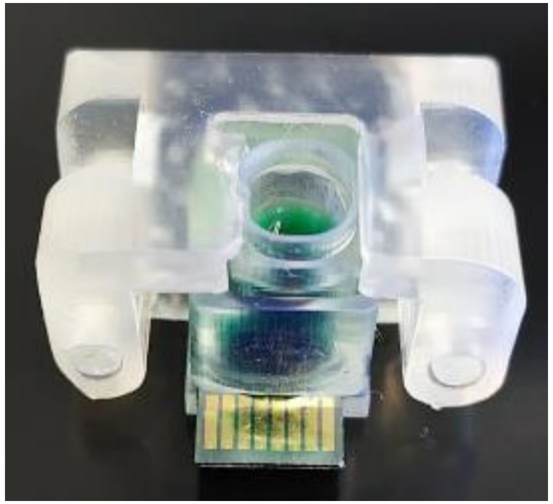


Simulation showing effect of flow CG mode



Food dye to show channel outline

System Integration



2021. IEEE Sensors, DOI: 10.1109/JSEN.2020.3021941

Summary

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Eliminate need for of addition of reagents:
Nanosensor design to locally control the chemistry of the solution at the sensor, e.g. pH control and minimising interferents by other species

Stabilising On-chip reference electrodes:
developing deposition methods for polymer coatings to maintain chemical stability

Electrochemistry that identifies chemical species:
developing tailored surface chemistries

Portable system for field measurements/ decision support systems (DSS):
Integrated sensor/electronics system for in-field measurement trials

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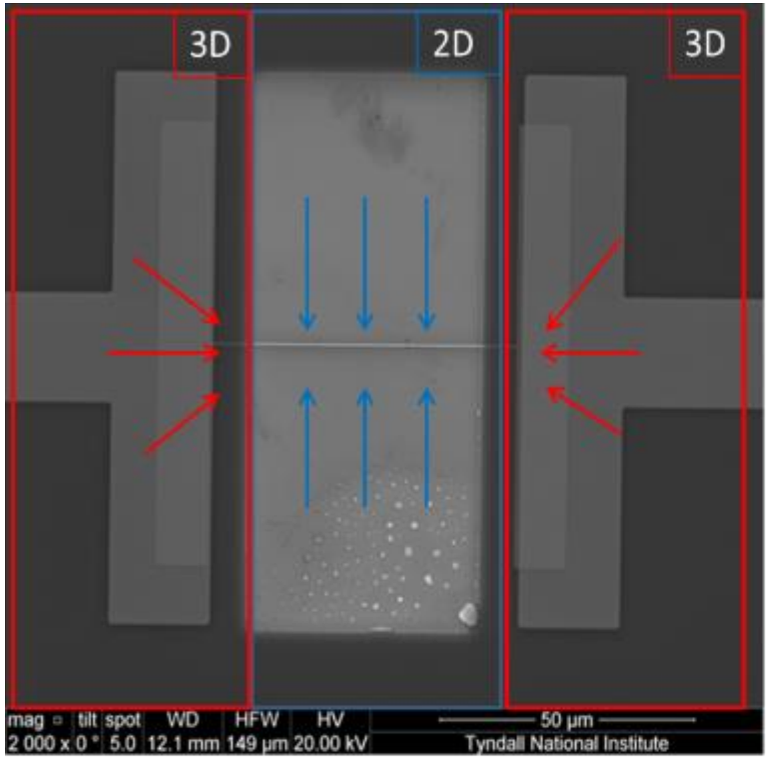
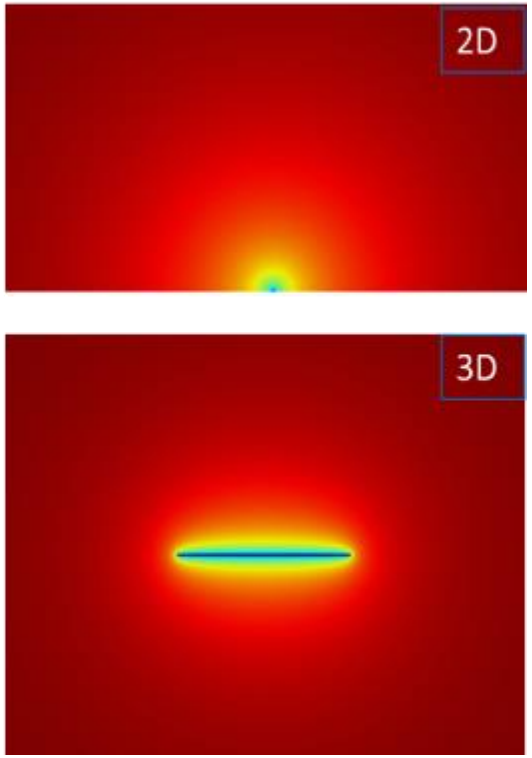
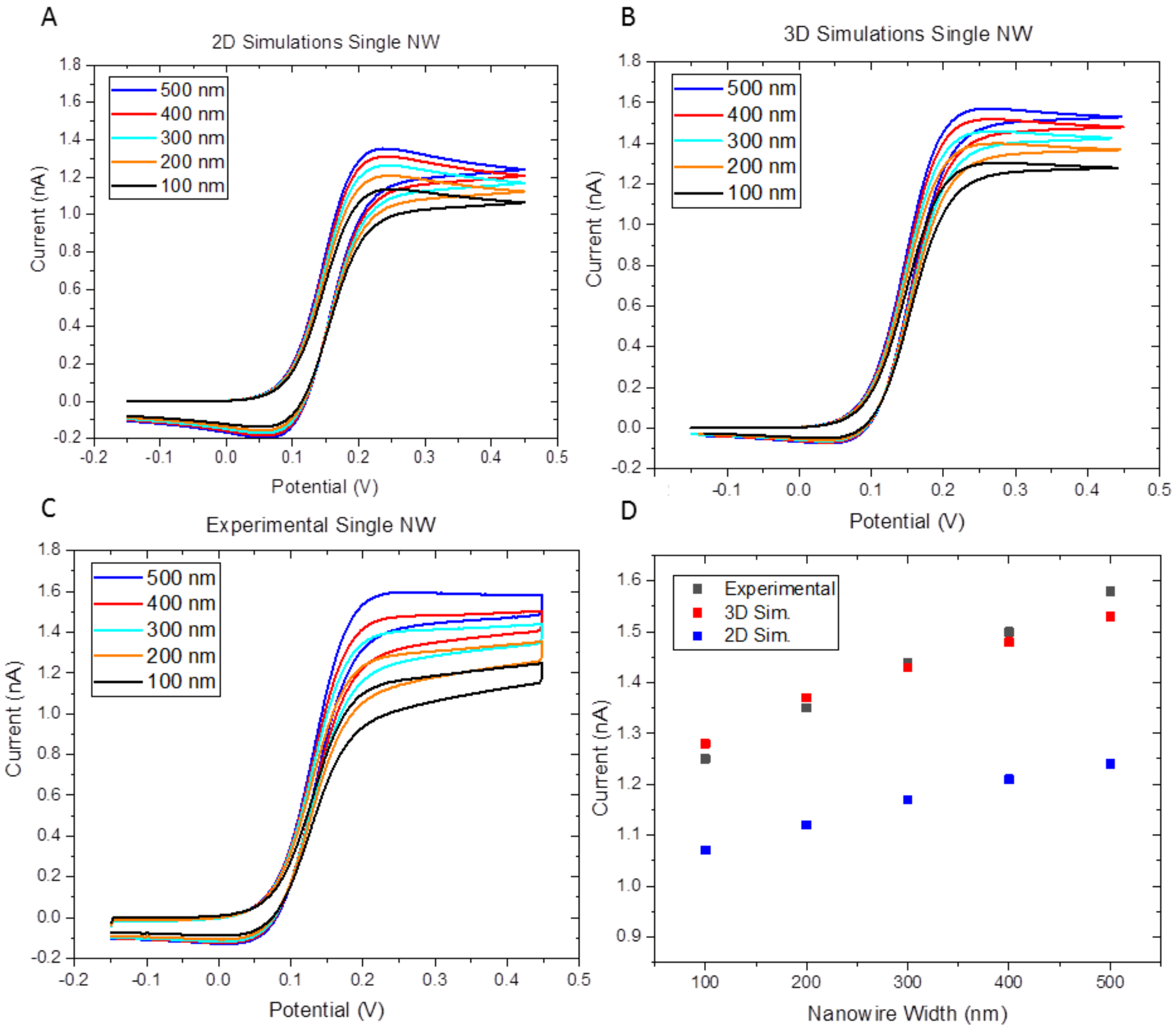
University College Cork, Ireland
Coláiste na hOllscoile Corcaigh

Rialtas na hÉireann Government of Ireland
Tionscadal Éireann Project Ireland 2040
Ireland's European Structural and Investment Funds Programmes 2014-2020
Co-funded by the Irish Government and the European Union
European Union European Structural and Investment Funds

2D v 3D simulations





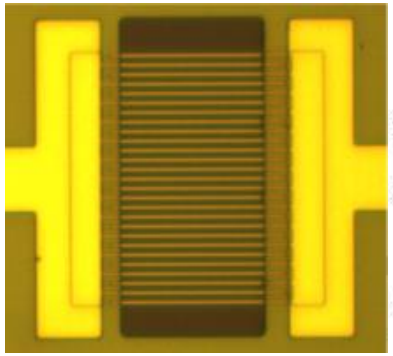


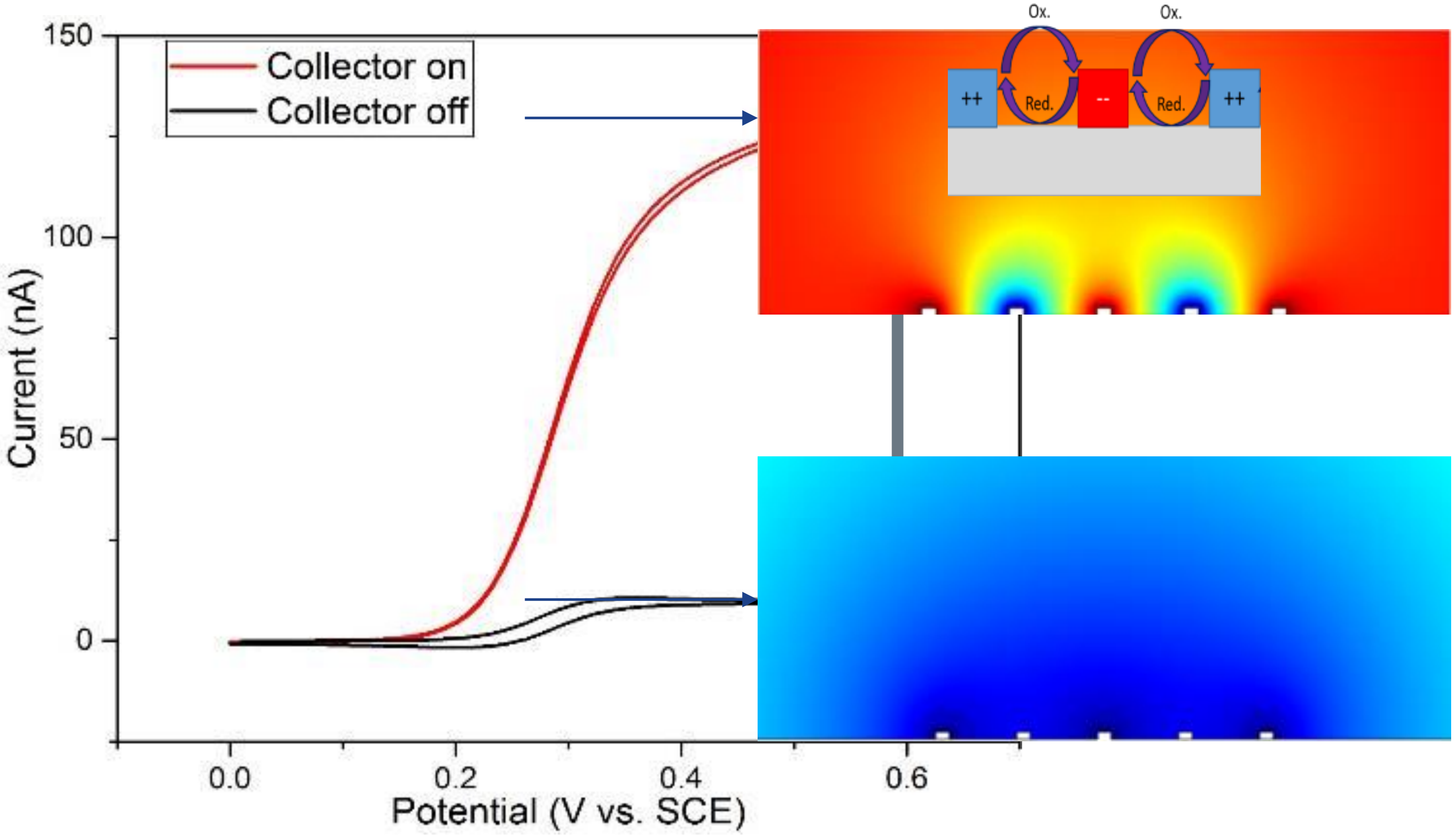
2022. Electrochimica Acta, DOI: 10.1016/j.electacta.2022.139890

Generator-Collector Devices

Addition of a collector bias of 0 V

Redox cycling occurs – Radial diffusion

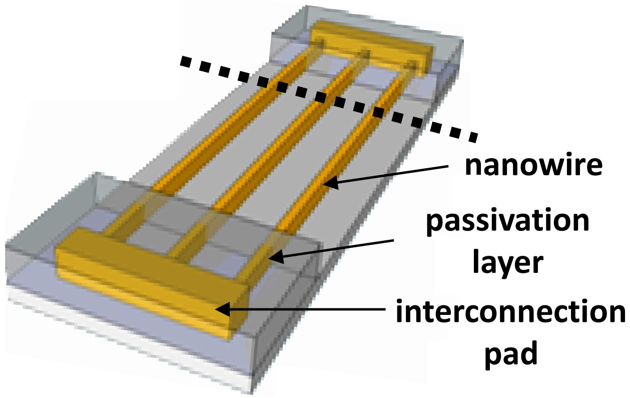


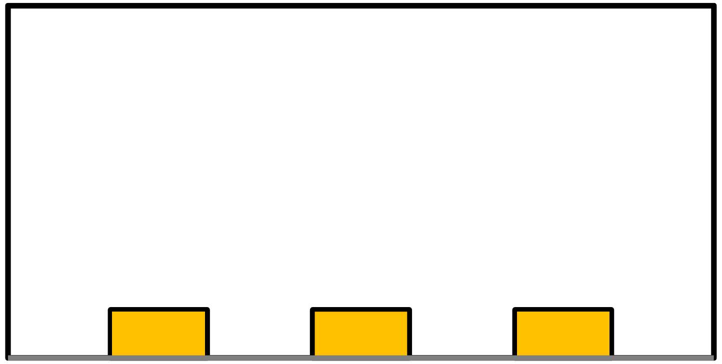


Overlapping diffusion layers – Planar diffusion

2018. Electrochimica Acta, DOI: 10.1016/j.electacta.2018.04.181

Nanowire Arrays – Electrode Pitch





- Three nanowires: 100 nm width x 50 nm height separated by ***d***
  - effect of altering inter-electrode distance using cyclic voltammetry
  - ***d* = 5 to 15 µm**

- Simulated concentration profile of 1 mM FcCOOH in 10 mM PBS at the electrode surface:

$$C_R(t) = \frac{C_R^*}{1 + exp\,[\frac{nF}{RT}\left(E^0 - E(t)\right)]}$$

  - depends on the applied potential
  - depends on the potential scan rate
  - target high scan rate (5000 mV.s^{-1}) since it allows rapid data capture