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Development of Electrochemical Sensors Based on Electrosynthesized Ion Imprinted Polymers for Cobalt (Co^{2+}) Ions Determination in Water

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L'Ateneo tra i due mari

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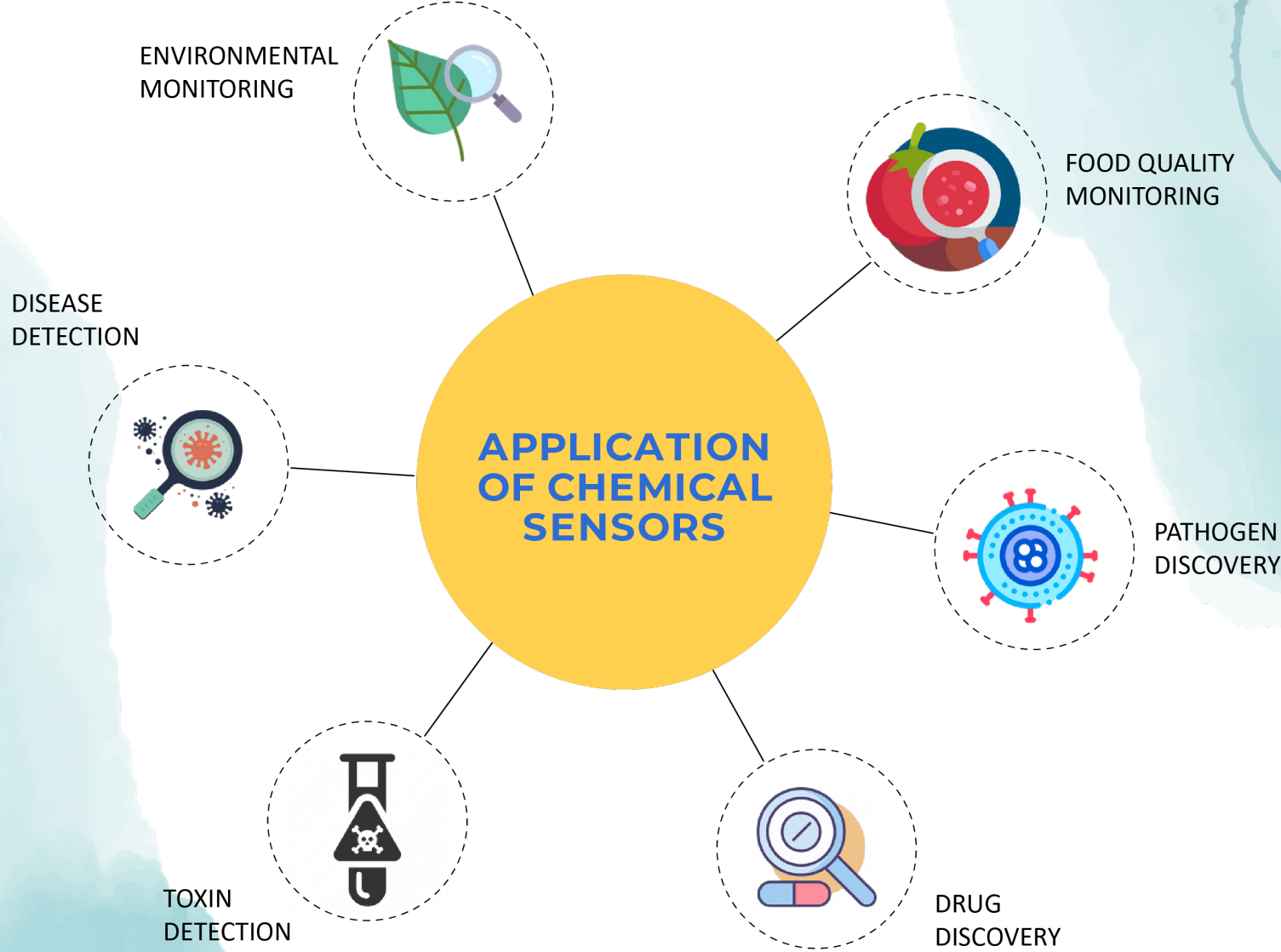


CONTENT

- ✓ INTRODUCTION
- ✓ OBJECTIVE
- ✓ METHODS
- ✓ RESULTS
- ✓ CONCLUSIONS

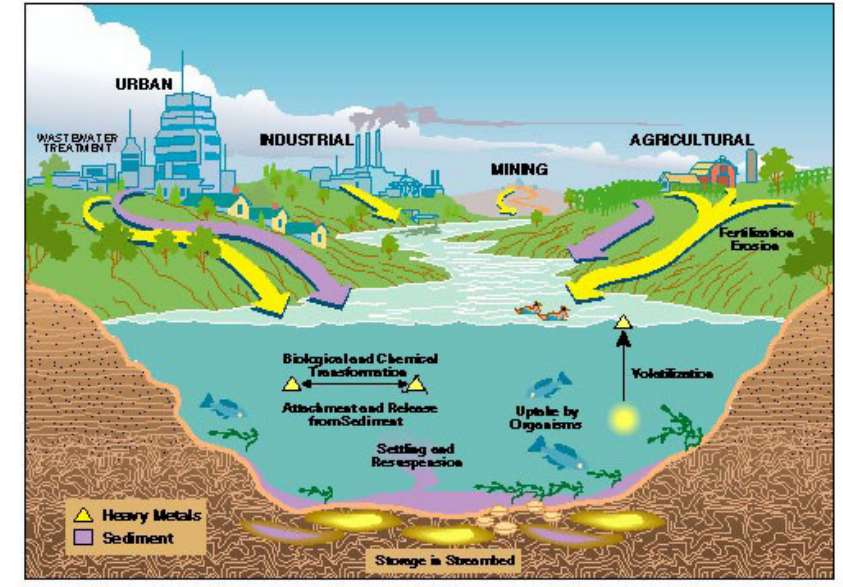


INTRODUCTION



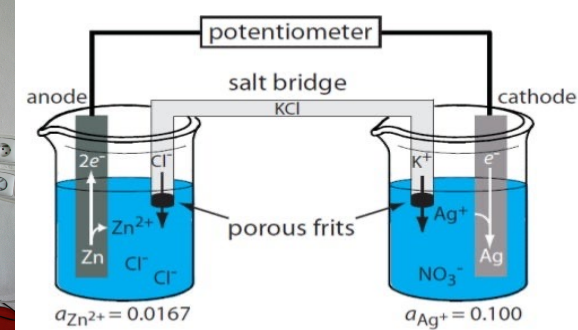


- ✓ **COBALT POLLUTION IN SOIL AND WATER**
- ✓ **MINING INDUSTRY, DOMESTIC AND INDUSTRIAL WASTEWATER, BURNING OF FOSSIL FUELS**
- ✓ **AFFECTS GROWTH AND YIELD OF AGRICULTURE CROP PLANTS**
- ✓ **POTENTIAL RISK TO FOOD SOURCES AND HUMAN HEALTH**
- ✓ **MONITOR EVEN TRACE AMOUNTS OF COBALT**



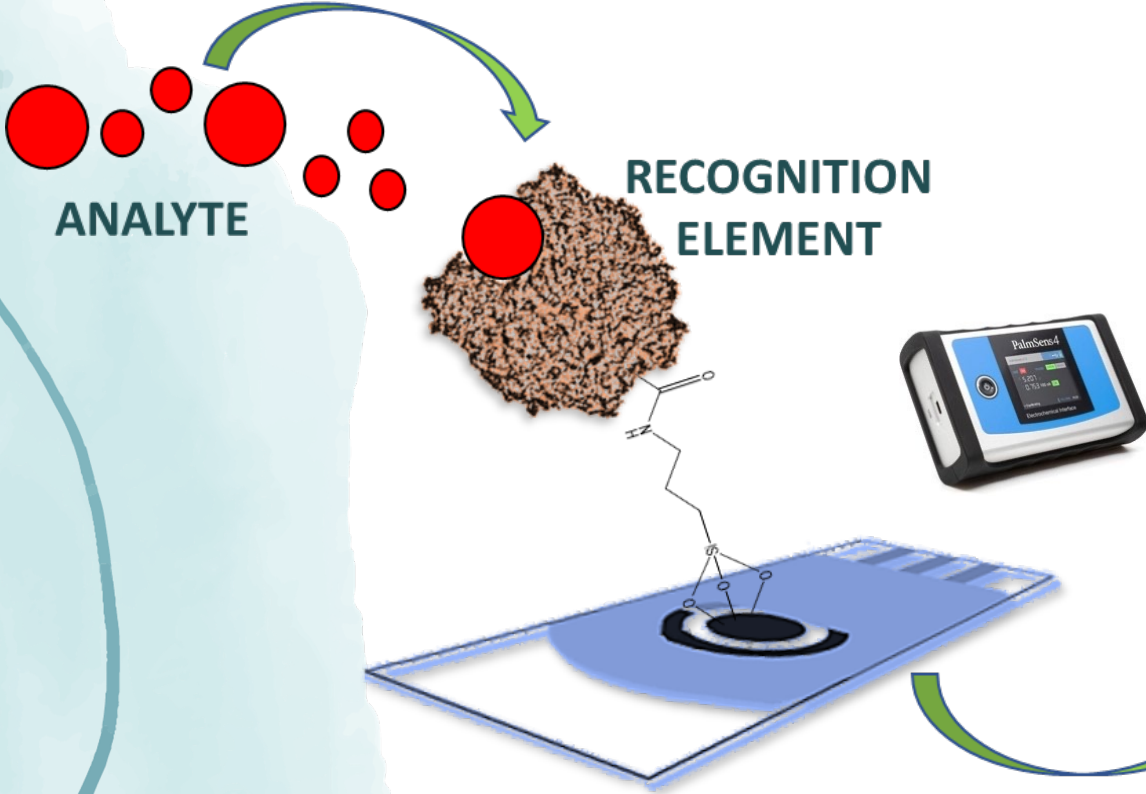


- ✓ **ATOMIC ABSORPTION SPECTROMETRY**
- ✓ **INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY**
- ✓ **FLUORESCENCE METHODS**
- ✓ **ELECTROCHEMICAL TECHNIQUES**
- ✓ **INTERFERENCE, SAMPLE PREPARATION, BEING TIME-CONSUMING, EXPENSIVE INSTRUMENTS, AND LOW SENSITIVITY.**
- ✓ **SIMPLE, RAPID, SENSITIVE, AND SPECIFIC METHOD FOR DETECTING Co^{2+}**

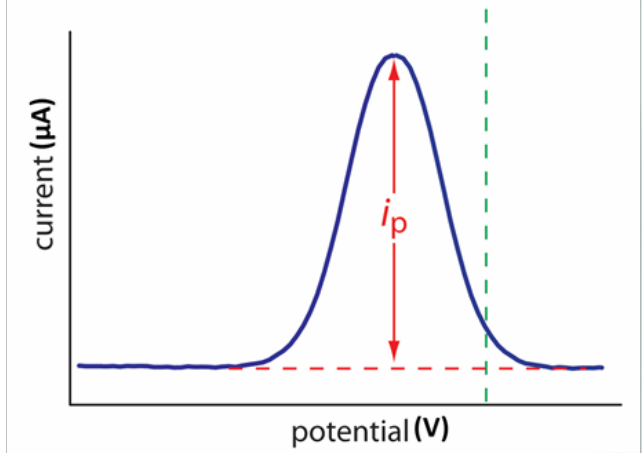




CHEMICAL SENSOR: A SCHEME



OUTPUT (SENSOR RESPONSE)






RESPONSE EXAMPLE OF A VOLTAMMETRIC SENSOR

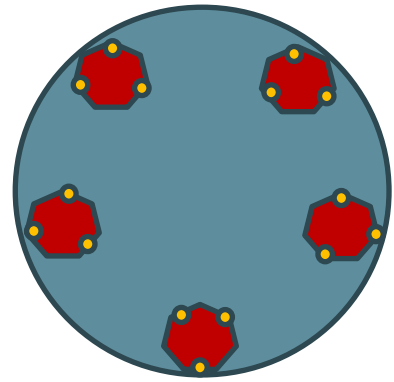


AN HIGH SELECTIVE RECOGNITION ELEMENTS: ION IMPRINTED POLYMER (IIP)

CHEMICAL SYNTHESIS

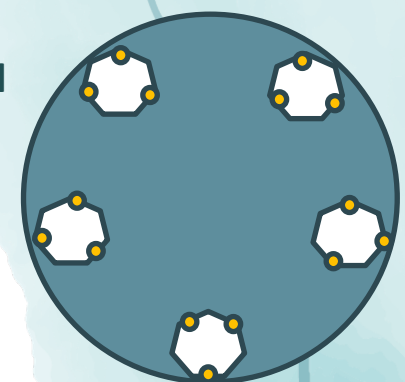
-  MONOMER
-  TEMPLATE, Co^{2+}
-  CROSS-LINKER

Activators
→





Particles of IIP + Co^{2+}

Template removal
←
→
Rebinding

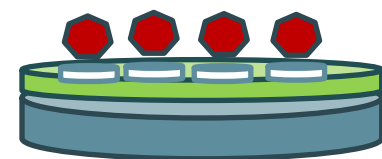


Co^{2+} - IIP
(particles and nanoparticles)

ELECTROCHEMICAL SYNTHESIS

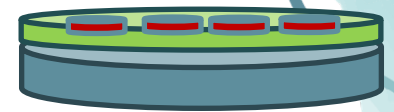
-  ELECTROACTIVE MONOMER
-  TEMPLATE, Co^{2+}

Potential (V)
→



Film of IIP + Co^{2+}

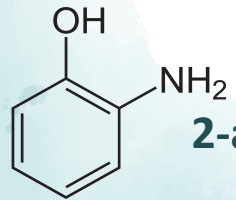
Template removal
←
→
Rebinding



Co^{2+} - IIP film



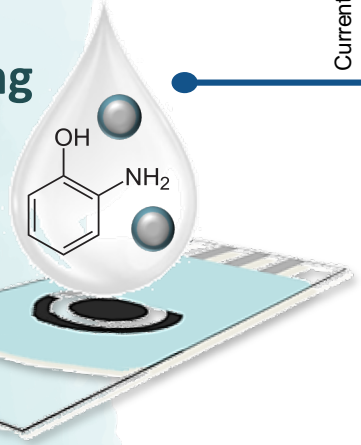
DEVELOPMENT OF AN ELECTROCHEMICAL IMPEDIMETRIC SENSOR BASED ON AN ION IMPRINTED POLYMERIC FILM FOR THE DETERMINATION OF Co^{2+} IONS IN WATER OF ENVIRONMENTAL INTEREST



2-aminophenol monomer

Co(II) ions

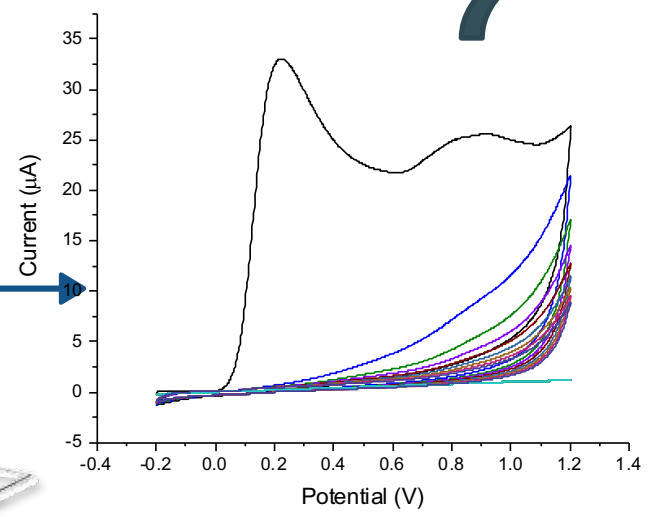
Drop-casting



Screen-printed carbon electrodes, SPCE

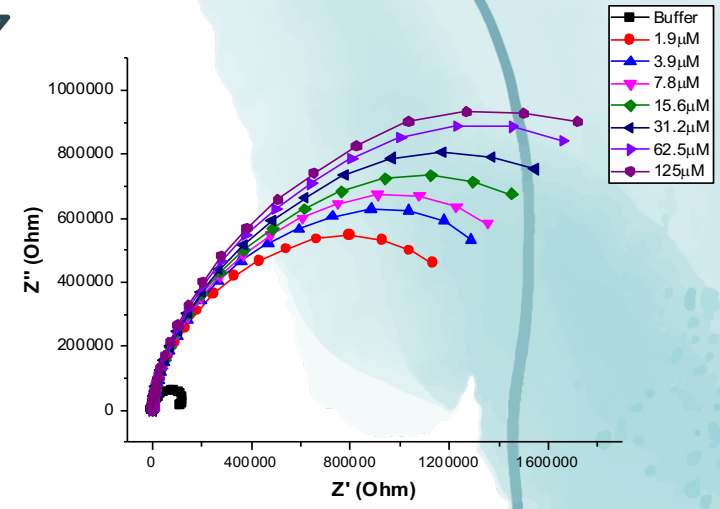
Cyclic voltammetry

Washing step



Electrochemical synthesis of ion imprinted polymeric film based on polyaminophenol (Co(II)-IIP film) and not imprinted polymeric film (NIP film, control)

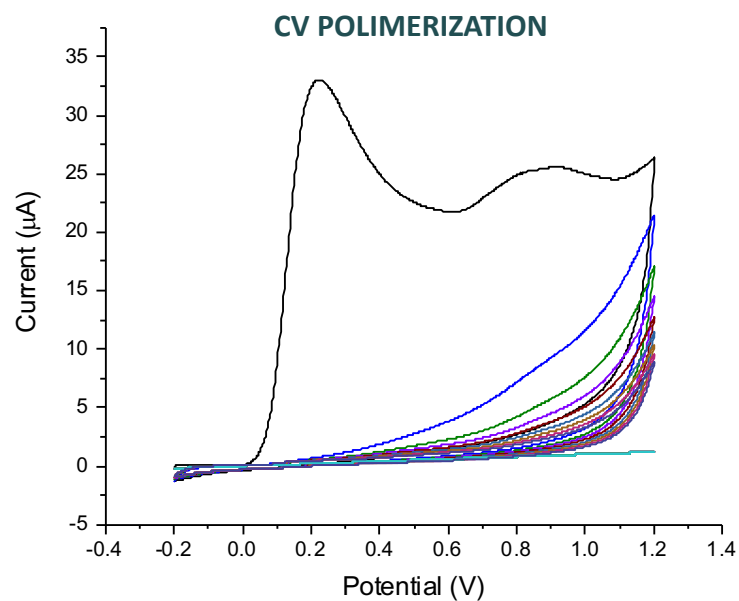
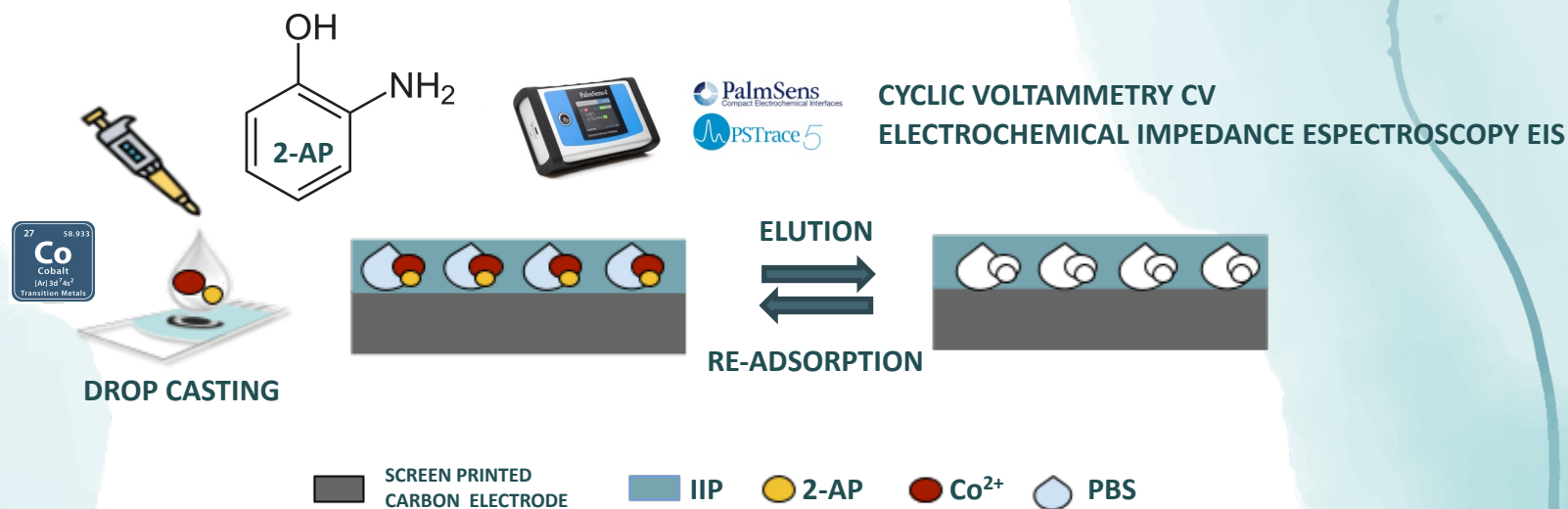
Electrochemical Impedance Spectroscopy



Analytical performances of IIP film and NIP film

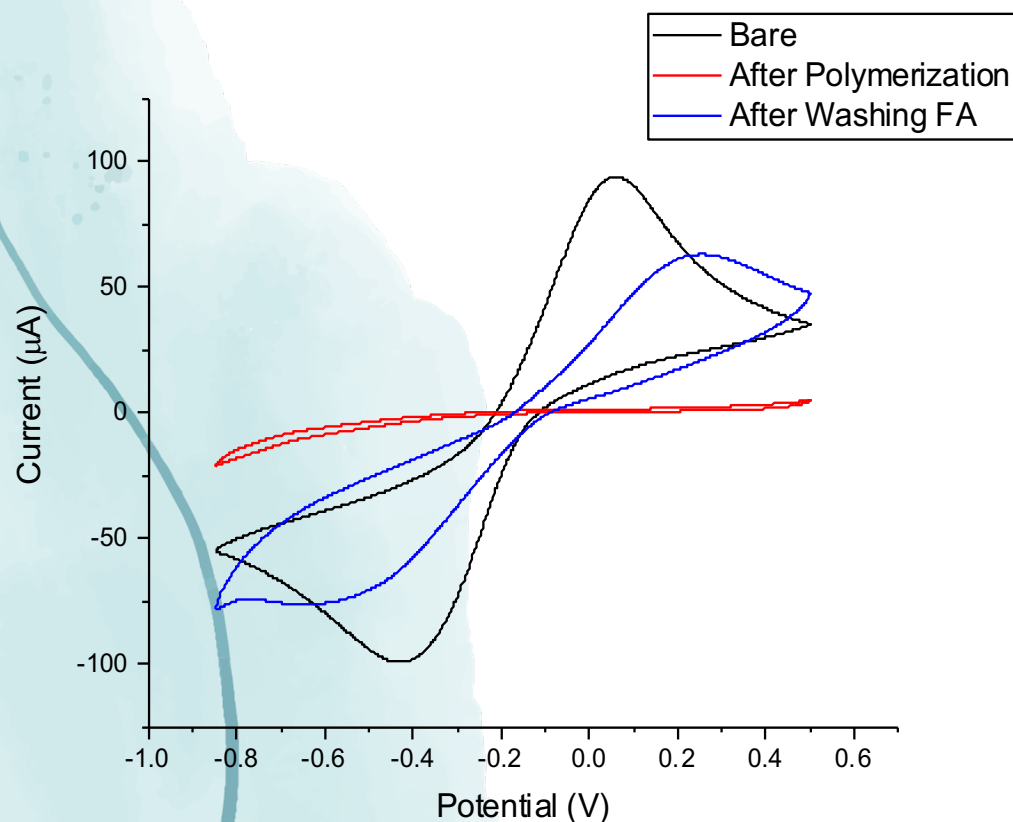
METHODS

Ion Imprinted Polymer (IIP) Preparation and Characterization

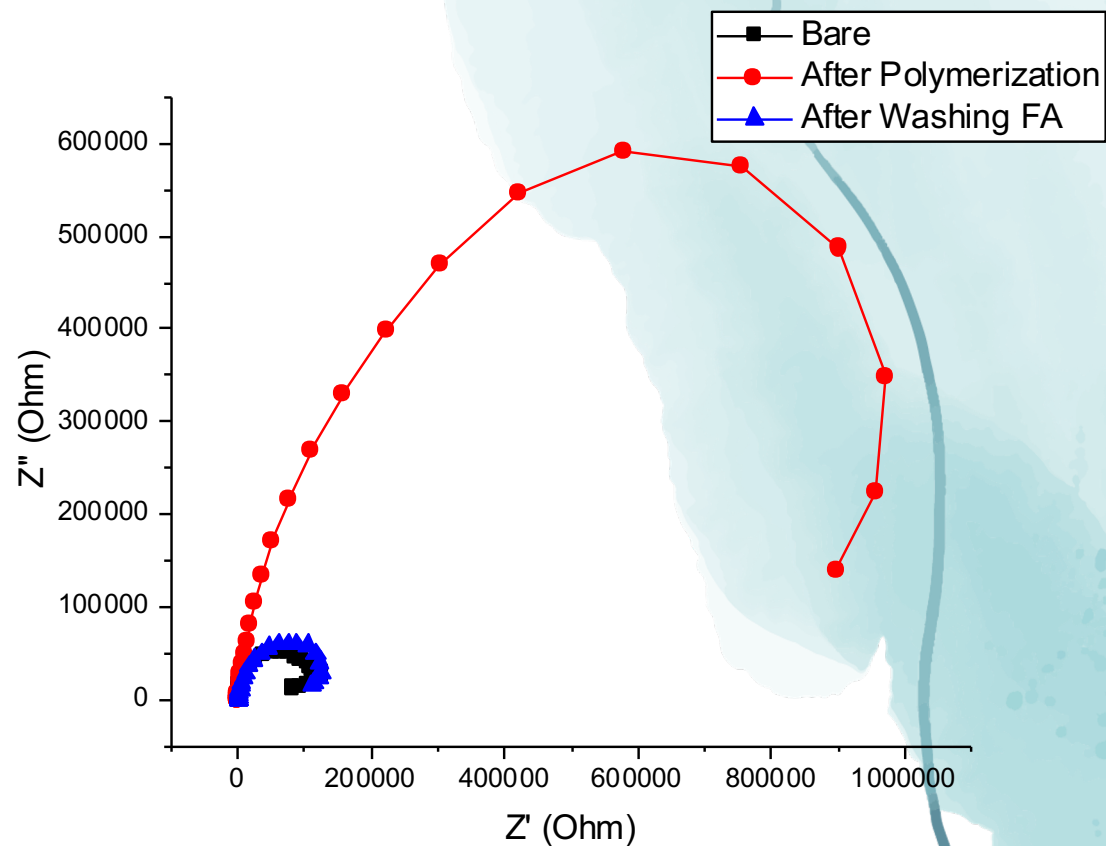




ELECTROCHEMICAL CHARACTERIZATION



Cyclic voltammetry in 10 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ + 0.1 M KCl for bare screen printed electrode, after 2-AP electropolymerisation and after washing step in formic acid:water 1:1



EIS data in 10 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ + 0.1 M KCl for bare screen printed electrode, after 2-AP electropolymerisation and after washing step in formic acid:water 1:1

OPTIMISATION BY MULTIVARIATE EXPERIMENTAL DESIGN

MODDE®
SARTORIUS



DoE

23 different experiments, 4
affecting variables

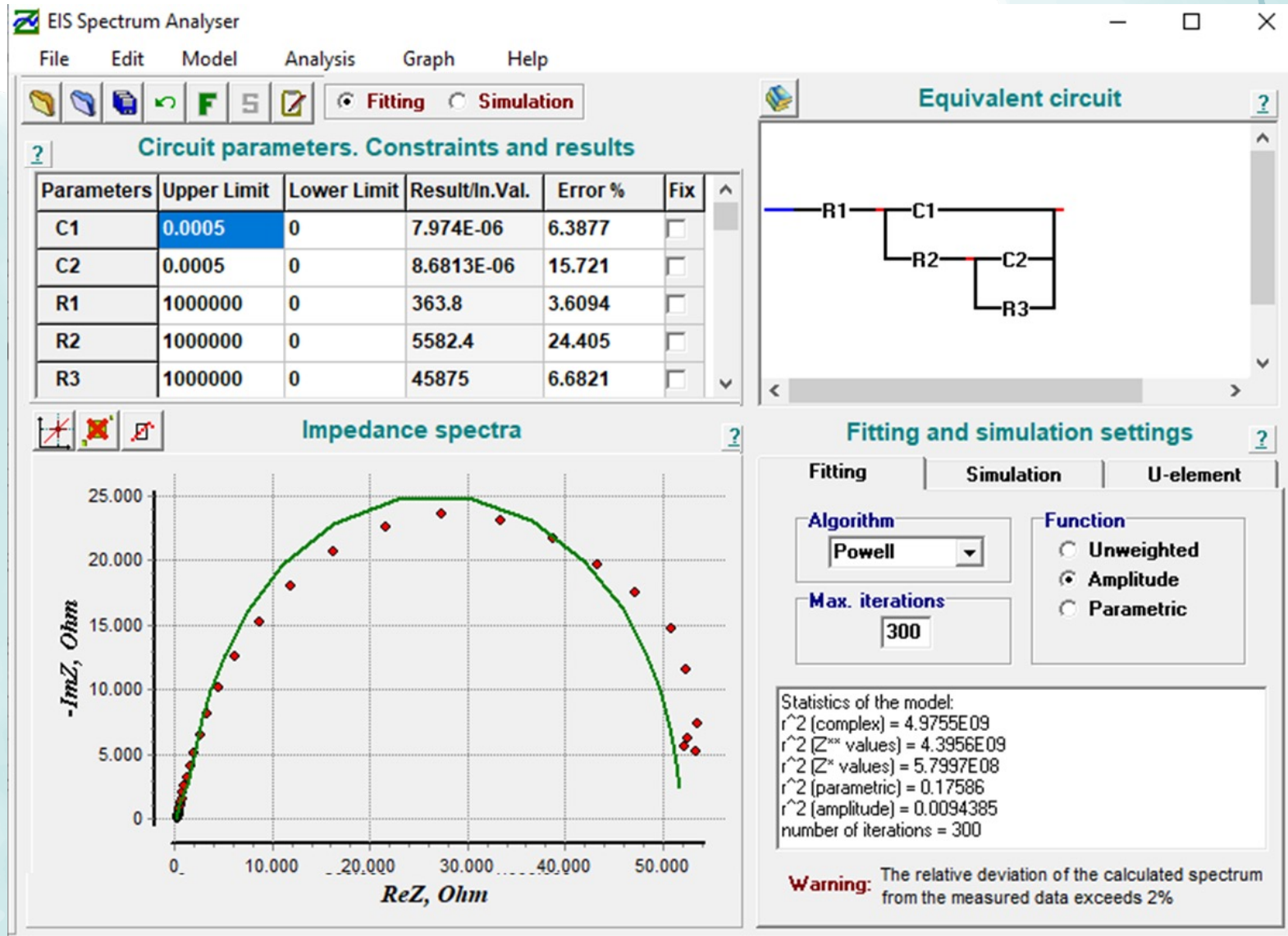
Y = Sensitivity of IIP sensor

Experiment number	Experiment name	Run Order	Incl/Excl	2-AP concentration	CO ²⁺ concentration	Cycles	Time elution
1	N1	18	Incl	1	1	10	10
2	N2	1	Incl	2	1	10	10
3	N3	5	Incl	1	5	10	10
4	N4	2	Incl	2	1	30	10
5	N5	23	Incl	1	5	30	10
6	N6	22	Incl	2	5	30	10
7	N7	3	Incl	1	1	10	25
8	N8	9	Incl	1	5	10	25
9	N9	6	Incl	2	5	10	25
10	N10	8	Incl	1	1	30	25
11	N11	16	Incl	2	1	30	25
12	N12	11	Incl	2	5	30	25
13	N13	19	Incl	1	3	20	17.5
14	N14	15	Incl	2	3	20	17.5
15	N15	20	Incl	1.5	1	20	17.5
16	N16	12	Incl	1.5	5	20	17.5
17	N17	4	Incl	1.5	3	10	17.5
18	N18	17	Incl	1.5	3	30	17.5
19	N19	7	Incl	1.5	3	20	10
20	N20	14	Incl	1.5	3	20	25
21	N21	13	Incl	1.5	3	20	17.5
22	N22	10	Incl	1.5	3	20	17.5
23	N23	21	Incl	1.5	3	20	17.5

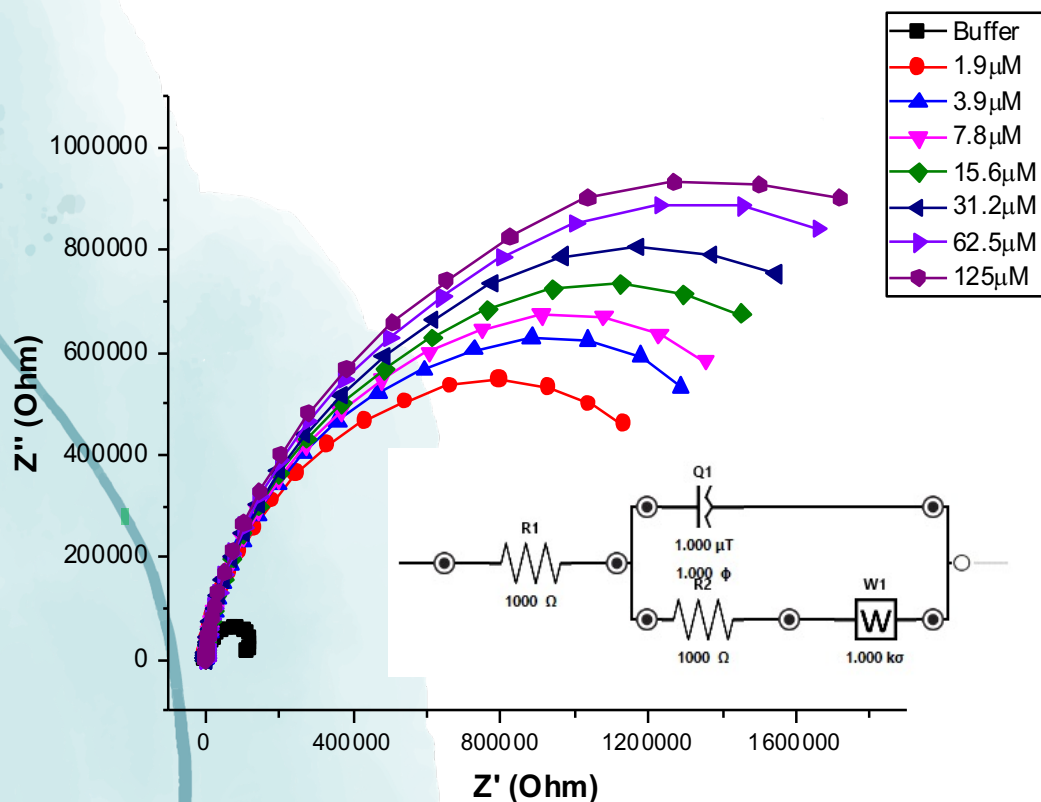
OPTIMISATION OF EXPERIMENTAL FITTING OF EIS DATA



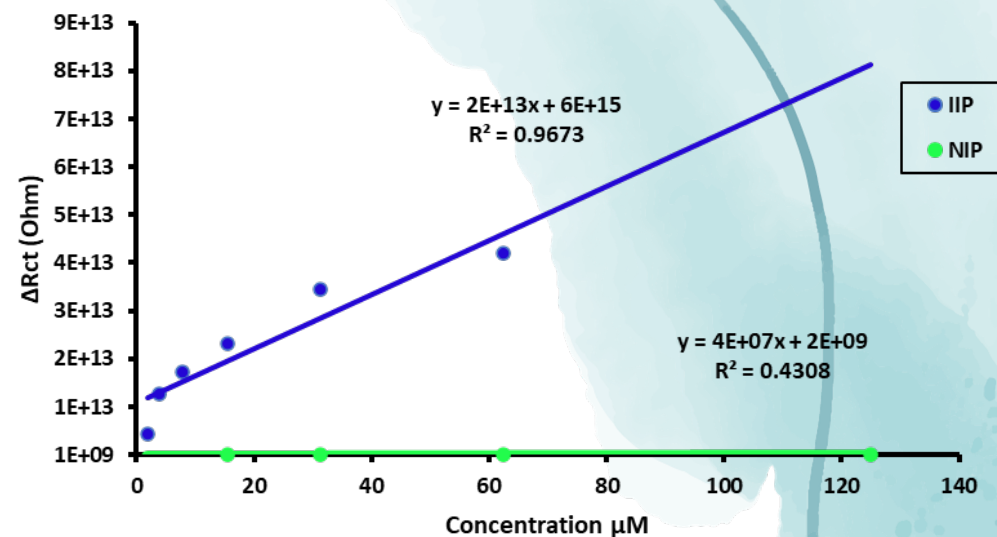
EIS Spectrum Analyser®



OPTIMISATION OF EIS DATA



Nyquist plot acquired in 10 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ for Co(II)-IIP film after incubation of Co(II) ions dissolved in acetate buffer solution (50 mM, pH= 5.0) at different increased concentration (from 1.9 to 125 μM)



Good reproducibility and expected trend have been recorded with a printed factor (IF=5) with high sensitivity



CONCLUSIONS

- ✓ Adequate properties of selectivity and stability of the IIP films, compared with the yields obtained with other sensors.
- ✓ 44% of experiments with best fit comparing circuit model vs. experimental data.
- ✓ Sensitivity of Co(II)-IIP film sensor towards Co^{2+} ions in the range of concentration between 1.9 and 32.5 $\mu\text{mol L}^{-1}$ was 5 times higher than that reported for NIP film, revealing the goodness of imprinted process.



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Thank you

