Machine Learning-Driven Calibration for Reusable Electrochemical Sensor Electrodes

Khitem Lahbacha[1,2], Francesco Siconolfi[1,2], Luca Tari[1,2], Gabriele Cavaliere[1,2,3], Antonio Licheri[4], Laura Micheli[4] and Antonio Maffucci[1,2]
[1]*Department of Electrical and Information Engineering, University of Cassino and Southern Lazio, Cassino, 03043, Italy*
[2]*EUT+ Institute of Nanomaterials and Nanotechnologies (EUTINN), European University of Technology, European Union*
[3]*Department of Information and Electrical Engineering and Applied Mathematics, University of Salerno, Fisciano, 84084, Italy*
[4]*Department of Chemical Sciences and Tecnologies, University of Rome Tor Vergata, Via della Ricerca Scientifica 1, 00133, Rome*
{khitem.lahbacha, francesco.siconolfi, luca.tari, gabriele.cavaliere, maffucci}@unicas.it
laura.micheli@uniroma2.it, antonio.licheri@students.uniroma2.eu

***Abstract*— Electroanalytical techniques detect analytes by measuring electron transfer during redox reactions. Screen-printed electrodes (SPEs) provide a low-cost, disposable platform for these analyses but are usually designed for single use, which raises sustainability concerns. This study investigates the use of machine learning to extend the usability of SPEs in chronoamperometric (CA) measurements. A Kernel Naïve Bayes classifier was applied to analyze full CA curves and classify analyte concentrations. Unlike traditional linear regression calibration, which often requires multiple electrodes per concentration, this approach aims to reduce material waste while maintaining analytical accuracy. Using repeated measurements across various concentrations, the model achieved an accuracy of 75.7%. These results demonstrate the potential of data-driven methods to enhance both the sustainability and efficiency of electrochemical sensing platforms.**

Keywords— Machine Learning, Chemical Analysis, SPE, CA, Pollutants, Wastewater.

I. INTRODUCTION

Electroanalytical techniques allow for the detection and quantification of chemical species by measuring electron transfer during redox reactions [1]. Screen-printed electrodes (SPEs) have emerged as a low-cost, disposable alternative to traditional electrodes, offering scalability and versatility for applications such as environmental monitoring and water quality assessment [2]. However, their single-use nature raises concerns about sustainability, particularly in large-scale deployments where material waste and production costs can be significant.

This study investigates whether machine learning techniques can help address these issues by extending the usability of individual SPEs. Traditionally, chronoamperometric measurements rely on multiple electrodes per concentration level to construct calibration curves from averaged steady-state currents. Here, an alternative approach is proposed, using repeated measurements from a single electrode and machine learning analysis to maintain performance while reducing electrode consumption. The aim is to promote more sustainable electrochemical sensing without compromising accuracy.

II. MEASUREMENT METHODOLOGY

A. *Instrumentation and Test Setup*

To evaluate the electrochemical performance of the graphite-based sensors, a series of chronoamperometric measurements was carried out using hydroquinone (HQ) as the target analyte. The sensors consisted of SPEs made of graphite, selected for their high electrical conductivity and chemical stability. Each sensor featured three electrodes: a working electrode (WE) where the redox reaction of HQ occurs, a reference electrode (RE) to maintain a fixed and stable potential, and a counter electrode (CE) to complete the circuit and enable current flow. A constant voltage was applied to the working electrode using a PalmSens Sensit Smart BT potentiostat [3], as shown in Fig. 1. Once the potential was applied, the current generated by the oxidation of HQ was monitored over time. This oxidation reaction produces a measurable current that directly correlates with the HQ concentration in the solution.

A set of HQ solutions at varying concentrations (0.5, 1, 2, 3, 4, and 5 mM) was prepared, and the sensor response was recorded using three different SPEs. Each concentration was measured 20 times to ensure the reliability and reproducibility of the results. Prior to data analysis, the baseline signal obtained from a blank sample (a solution without HQ) was subtracted to remove background noise and isolate the signal attributed to the analyte. The aim was to obtain clear and stable current plateaus for each concentration, which are essential for constructing accurate calibration curves.

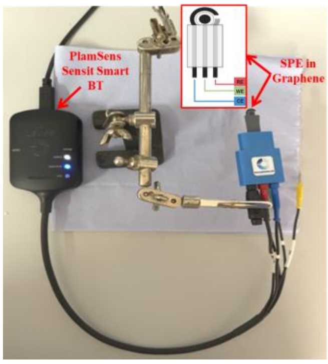


Fig. 1. Measurement setup highlighting the 3 connectors of the SPE.

B. *Preliminary Results*

The results displayed in Fig. 2 show the CA responses for 2 mM of HQ solution, recorded at the 1st,5th,10th,15th, and 20th measurements. The current curves all follow the typical pattern of a CA test with a quick peak at the beginning, followed by a smooth drop and then a stable plateau. This indicates that the oxidation of HQ happens quickly once the potential is applied, and then the system stabilizes as the reaction reaches equilibrium. Over tests and considering the same electrode, the current plateau shows a slight decrease, due to natural SPE degradation.

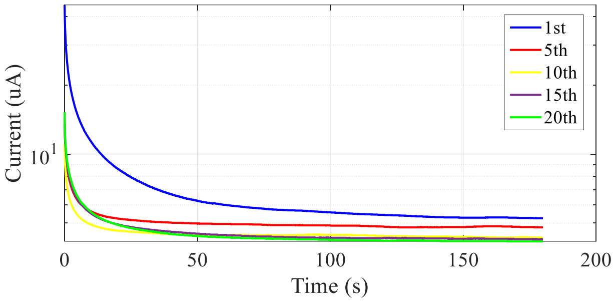


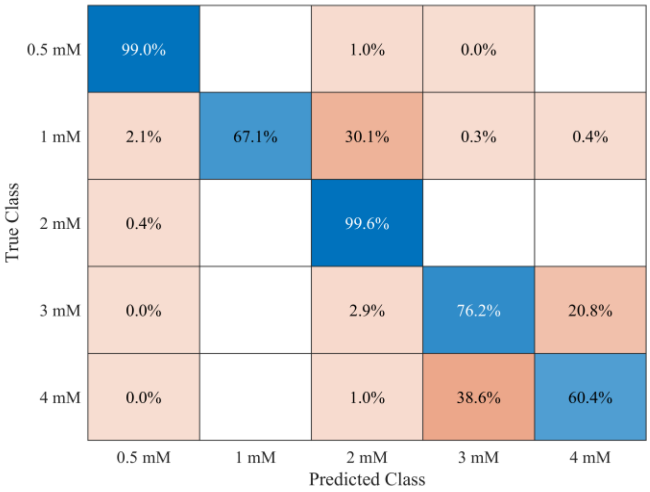
Fig. 2. CA measurement response of HQ at 2 mM, showing data from the 1st,5th,10th,15th, and 20th measurements.

III. Prepare Proposed Method and Results

As demonstrated in Section II, traditional analytical methods exhibit a progressive loss of accuracy due to increasing variability in measurement outputs after repeated sensor usage. To explore the potential for reusing SPE without significant performance degradation, CA response curves were employed as input features in a supervised classification framework. In particular, a Kernel Naïve Bayes (KNB) classifier was selected following a comparative evaluation of several algorithms using MATLAB's Classification Learner App. The Kernel Naïve Bayes classifier is a probabilistic model that extends the classical Naïve Bayes algorithm by incorporating kernel density estimation to model the probability distribution of the features. This hybrid approach improves classification performance while maintaining a low computational cost, making it suitable for resource-constrained scenarios such as disposable sensor applications. The measurement data of the CA collected during the testing campaign were organized into a dataset for model training, validation, and testing. In the first analysis, data from the first two SPEs at each concentration (each with 20 repeated measurements) were used to create the training and validation datasets, while the third SPE served as an independent test set.

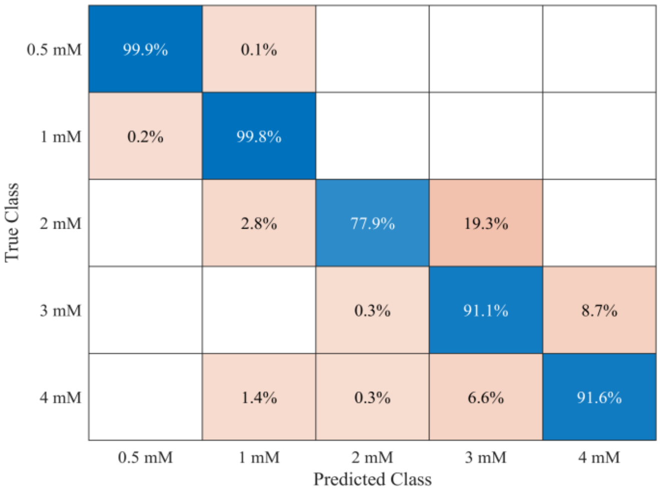
The training dataset included measurements from 10 electrodes, distributed across five different concentration levels (i.e., two electrodes per concentration). A 5% subset of the training data was withheld and used for validation through 5- fold cross-validation. The test dataset comprised the remaining measurements obtained from the third electrode, covering all 20 repetitions at a single concentration level. Fig.3 presents the classification results obtained for all 20 measurements from the test electrode, achieving an average classification accuracy of 75.7%. Applying a majority voting criterion across the 20 predictions yielded a correct identification of the target class, supporting the feasibility of the proposed method as a preliminary proof of concept.

To further investigate performance, an alternative strategy was explored in which the classifier was incrementally retrained using data from the same electrode every four tests. This retraining scheme was designed to mimic real-time adaptation and compensate for potential electrode degradation. Preliminary results indicate that this adaptive approach outperforms conventional recalibration strategies based on linear models. For instance, Fig.4 illustrates a case where the model was retrained after the eleventh test and subsequently evaluated on measurements from twelfth to fifteenth. These findings will be further expanded and validated in the final submission.



	0.5 mM	1 mM	2 mM	3 mM	4 mM
0.5 mM	99.0%		1.0%	0.0%	
1 mM	2.1%	67.1%	30.1%	0.3%	0.4%
2 mM	0.4%		99.6%		
3 mM	0.0%		2.9%	76.2%	20.8%
4 mM	0.0%		1.0%	38.6%	60.4%

Fig. 3. Classification Accuracy training 20 electrodes.



	0.5 mM	1 mM	2 mM	3 mM	4 mM
0.5 mM	99.9%	0.1%			
1 mM	0.2%	99.8%			
2 mM		2.8%	77.9%	19.3%	
3 mM			0.3%	91.1%	8.7%
4 mM		1.4%	0.3%	6.6%	91.6%

Fig. 4. Classification Accuracy retraining at 11th test and testing from 12th to 15th.

Acknowledgment

The research leading to these results has received funding from the Project P2022CZA3P "Dress The future: novel combined wearable integrated systems", funded by EU in the NextGenerationEU through the Italian Bando PRIN 2022 PNRR, D.D. n. 1409 del 14.9.2022, by MUR (2023-2025).

References

[1] Scholz, Fritz, and A. M. Bond. "Electroanalytical methods: guide to experiments and applications." (2002).

[2] Molinara, M., et al. "A deep transfer learning approach to an effective classification of water pollutants from voltammetric characterizations" , IEEE 21st Mediterranean Electrotechnical Conference (MELECON), 2022.

[3] PalmSens BV. Sensit Smart BT User Manual https://www.palmsens.com/knowledgebase-article/sensit-bt-operator-manual/