CA-125 Detection Using Micro-Fluidics With An Implementation of the Latest Machine Learning Algorithms

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Abstract: Electrochemical sensors are very sensitive and accurate detection mechanism for the detection of tumor biomarkers in fluids such as blood, bodily secretions and urine. They detect low analyte concentration very accurately and in real time by electrochemical reaction and low biomolecular interactions. These sensors are vital in oncology for the early detection of cancers in the human body. The forward scan of the cyclic voltammogram is modelled using machine learning algorithms. Machine learning is known to provide an in-depth study of the curve, which cannot be done with a normal human study. Humans can only predict a determined value using small measurements. Still, a machine, when trained, can extract what the time of the reaction was, how fast it occurred, whether it happened successfully or there was an adverse condition at the electrodes, what was the concentration of the sample. The curve provides a detailed breakdown of the entire process and reaction. A machine, when trained in this case and many others, is the key to understanding the inner workings of complex processes. Electrochemical sensors can detect biomarkers with high sensitivity, aiding early cancer diagnosis and treatment monitoring. Tuning with machine learning adds to the overall efficacy and strength in this detection. When anything happens it may be Covid-19, cancer or any disease it is best when it is detected early, late detection is never warranted. Late detection leads to complicated procedures, painful surgeries and traumatic experiences. This is the reason we are promoting early detection of the CA-125 biomarker by promoting machine learning usage in electrochemical cyclic voltammogram system.

Keywords: Cyclic Voltammogram; Machine Learning; Forward Scan; Cancer antigen- 125 ; Channel

I. Introduction: When anything happens, it is best when it is detected as soon as it occurs. It may be COVID-19, any abnormality, any disease, specifically cancers, whose survival percentage is maximum when it is detected at the first stage, and the detection in the last stage is the last thing sought or an unfortunate thing. A patient can be 97% saved when it is detected in the first stage, while the survival percentage reduces to less then 20% when detected in stage IV, as confirmed by studies in [1], [2], [3], [4], [5]. Chemotherapy is the last sought-after thing, and anti-cancer therapies, as in [6], have been advantaged. In this research, there is an introduction to cancer antigen 125 element detection at a first stage, but the other elements, like machine learning as well as the channel fabrication, are intricately defined at ease and with forwardness as a beginning to this area. Machine learning is generating heat due to its versatility of use. It enables the computer to respond to an input based on its training model, which is optimised based on the generated training data, which is fed into the model. Machine learning is garnering attention due to rapid advancements in hardware performance, which makes it feasible to be applied today. Compared to other problem solving techniques, machine learning shortens the task of attaining answers to complex problems, problems we barely understand with our human intelligence. This understanding comes to us only after training the machine learning models. The technologies touched by machine learning include speech recognition and computer vision. Moreover, although human cognitive intelligence is too complex to comprehend to understand or even to train these models but they are successful through deep neural network models. Machine learning is also applied to material sciences as in [7], [8]. Cyclic voltammetry is a strong candidate with a cyclic voltammogram extracted, which can be used in the accurate validation of sample concentration as in [9], [10], [11], [12], [13]. However, when AI-ML is integrated in studying these curves, it adds gravity and depth to the entire model and procedural detection as shown in [14], [15], [16], [17], [18], [19]. Machine learning is a very diverse area, and its applications are still more diverse. Training a machine to solve beyond human intelligence and beyond is a topic of wide discussion in computer science and interdisciplinary areas. It is how deep you can go into the depth of the training models and the perfection of the model. More in length the training models is the better the model is known. In this research paper introduction to more advanced models is provided with more accuracy and results that can extract as much as possible from the cyclic voltammogram curves. Cyclic voltammogram, as is well known, works in the forward and reverse scan during the two flip flops but only the forward scan data is used to extract the information which is of our interest in this machine learning implementation, while the reverse scan does have information of fouled electrode and adsorption and diffusion, but the reverse scan is not studied during the machine learning model training. Therefore, from the fundamental concepts, the reduction potential or reverse scan does not help much for the extraction of knowledge from this scan, as it is seen that in this scan, there is practically not much information change observed during this phase. Therefore, the majority of the information will be derived from the forward scan, which is of our prime interest in this paper and conceptually. Forward scan, as known, works with the oxidation potential of the electrode. It is here that the electrode donates an electron and gets reduced. It is also known that if an electrode gains an electron, then it gets oxidized which is the case in the reduction potential, with the case of the cathode. The anode gets oxidized. Machine learning and its related algorithms developed since the world war II, and today are very intricately and interactively developed. Today, they have etched their place practically in every field of research. Machine learning is not the thing only of computer science, and every field can derive benefits by using the results derived from this. Today, with the rapid development of machine learning models such as convolutional neural networks, recurrent convolutional neural networks and other machine learning models, which will be explained in this paper. Machine learning, as is well known, is extracting intelligence from the machines, which humans can do but much more than what humans can witness from the limited intelligence. It involves mathematics and concepts of various sciences, which help it to be developed. An attempt made in various research papers in machine learning is again reattempted in this research paper. Machine learning models have achieved their perfection by taking the best things from every science available outside, though not all, but some very distinct, useful ones. The best things are obtained by churning of things, as evidenced by all the developments in science and technology. Machine learning, through its multiple channels, has advanced significantly, leaving its fingerprint in almost all domains. In a method in [20] conventional cyclic voltametric stripping (CVS) limits both accuracy and efficacy. This often requires excessive reaction analytical time, and is practically not very suitable for in-situ applications. Machine learning techniques have emerged due to their ability to simultaneously extract the concentration of multiple additives from a single voltammogram curve. Without doubt, ML-based techniques improve accuracy and speed of detection in this overall method, but further advancement in the ML-based techniques is required at the development and training level. One of the ways of understanding the CV curves accurately with strength is by introducing them to ML techniques. ML techniques can analyse all the electrochemical data and the characteristics of each current-voltage (I-V) curve. The features of the I-V curves when trained lead to a sublime phenomenon of understanding, the behaviour of each additive can be factored in and processed to determine the concentration of each additive at each subsequent level. Traditional methods take hours to determine the concentration of the analyte and sample. Ml-based methods require a minute at most, i.e., as soon as the raw data is generated and fed into the algorithm, it soon provides us with the concentration of the sample, which is done in a couple of seconds. In a very recent study by Yoon et.al demonstrated that the decomposition of PEG's and the accumulation of the segment PEG's in the electrolyte can be effectively monitored by ML-based technique as shown in [21].

II. Related work: In a paper in [22], machine learning has solved electrochemical processes. In this paper, there is a profound discussion on this subject with subtle elements. Electrochemical sensors are vital for the advancement of drug improvement, testing and monitoring. Additionally, personalised medicine enables the precise identification and quantification of drugs. To achieve better performance, it is well accepted that they require a reduced loss function and architectures that require an understanding of the cyclic voltammogram, but during redox peaks. There is a general introduction of identQuantNet, which is an improved AI-based framework for the verification and validation of advanced drug testing using AI-ML. This involves processing the preprocessor and resultCombiner into the cyclic voltammogram electrochemical setup. During this entire setup, the technique is in the extraction of redox peaks in a single cyclic voltammogram that serve to feed the data to CV, which facilitates detection at the same time, utilising a dual-loss approach which balances precision with the clinical priorities, to reduce the estimations. In research done in [23] where electrochemical is well exploited in detection. They have exploited the accurate quantification of drug concentration using an artificial neural network (ANN). This has led to the development of point-of-care and wearable devices for biomedical applications. But the downfall in these methods is that most of the research and results only concentrate on the accuracy of how the predicted value is close to the accuracy or actual value, which technique is used in the detection of drug concentration. However, in this technique, the output loss function is optimized in the design of the ANN. It is noteworthy to mention that in this technique, mean squared error (MSE) and weighted mean square error (WMSE) are proposed for avoiding underestimation of drug quantification. Drug quantification by studying the redox peaks is done in papers in [15], [16]. Major work related to radiation was studied in [24], [25] where cancers are detected. In the paper in [26] beautiful explanation with implementation, makes this entire machine learning very versatile and in-depth at the same time. Previous work improvement is done from methodologies of work in the past from [27], [28], [29], [30], [31], [32], [33], [34], [35], [36], [37], [38], [39] into this paper. The work was started way back in 2018 as in [40] leading to more improvement as shown in [41], [42], [43], [44], [45], [46], [47], [48], [49], [50], [51], [52], [53], [54], [55], [56], [57]. Moreover, large datasets generated based on the estimation results open the possibility of training ML models for advanced drug quantification and other applications using electrochemical detection. Multiple drug interactions are taken into consideration.

III. Methodology: Sensor and data acquisition.

A Whatman grade 4 paper based channel is designed with four outlets to make the plasma flow to the detection region. Two glass slides are attached to the two almost extremities point to give it a strong foundation like support. The channels are designed as shown in figure below.

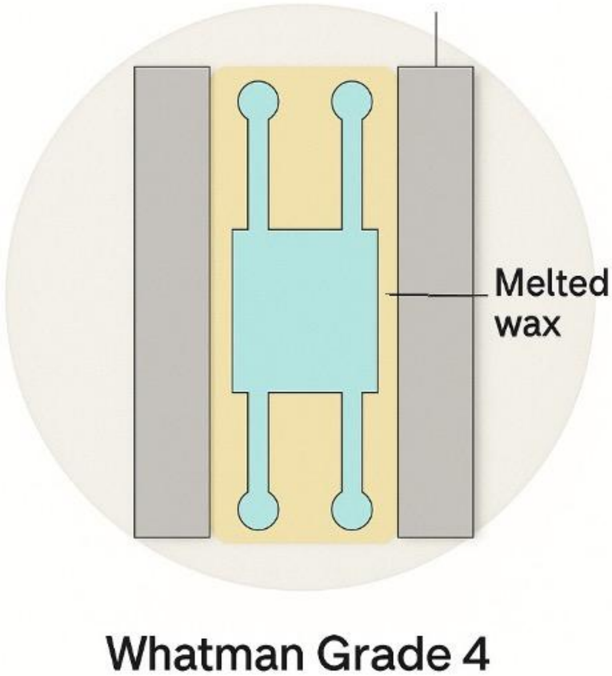

Figure 1: Our proposed whatman paper with four output channels

In cyclic voltmeter the detection takes place at the working electrode where the screen printed electrode (SPE) is attached to the anti-body and the detection sample to be investigated.

The four outlets helps in the detection of four biomarkers which are cancer antigen CA-125, Human epididymis protein 4 (HE4), carcinoembryonic antigen (CEA) and C-reactive protein.

Each methodology:

CA-125: Au nanoparticle is deposited on the SPE. Either Phosphate PO^{-4} or hydroxyl OH^{-1} is treated with the SPE to be later treated with the CA-125 antigen or antibody.

HE4: The HE4 detection is done by rinsing the SPE or working electrode with the chloroauric acid to be incubated for 30 minutes before being treated with HE4 sample. A value of less than 70 pmol/L is normal for premenopausal women and a value of 140 pmol/L or higher is normal for postmenopausal women while a value of 80 pmol/L or less is normal for normal men.

CEA: Proposed Molybdenum Sulphide (MoS_2) and Cobalt Oxide (Co_3O_4). MoS_2 helps in the activation of the surface and faster electron transfer during the reaction. Co_3O_4 helps in optimising the limit of detection, i.e. the lowest quantity of the sample can be accurately measured or is enhanced.

CRP: This is a liver-produced substance enhanced in patients with inflammation or tissue damage in the body. In this the electrode is MoS_2-Co_3O_4-Au NP, is used in which Molybdenum Sulphide enhances the surface area while Cobalt Oxide lowers LOD, and gold nanoparticle enhances the antibody aptamer immobilisation.

IV. Machine Learning Framework:

A. Data Processing and Model Implementation: The machine learning framework was implemented using Python-based using the major libraries available in python such as keras, tensorflow, numpy and pandas by recalling them and using them in this experiment in visual studio code.

The curves generated by the cyclic voltammogram was extracted into a CSV format and fed into the numpy library or code where the code generated the machine learning output.

The processed data was later fed into the machine learning algorithm which inherited keras library to perform over-fitting of this data to produce results.

This data-driven approach enables the model to learn important correlations between voltammogram shape characteristics such as slopes, curvature, and peak morphology which helps in the detection of the analyte concentration using machine learning.

B. Why Machine Learning is Important? Machine learning is well known to improve the way in which the results are studied, and the output is extracted. To a human, a cyclic voltammogram curve is only a curve; to an ML algorithm, it is a high-dimensional footprint of the chemical state of your electrode.
Machine learning is used as the curve contains a lot of hidden patterns in the curve which the human cannot extract by looking at. Humans are mechanical and don't have the capacity to sense minute details or patterns. Machines, when trained, can be a great instrument as agents in detection.
In cyclic voltammetry the shape of the curve, the curves, bends, slopes, peaks, and turning points, curvature and symmetry contains almost all the information of about: Mechanism, concentration, kinetics, diffusion, electron transfer rate, adsorption versus diffusion, capacitive behavior, electrode surface condition and adversarial conditions at the electrode. While the human eye only sees the peaks and peak position. A machine learning model can sense all the data from the curve.
The slope of current versus potential in different regions in the cyclic voltammogram reveals: how fast current rises (kinetics), whether diffusion is dominating, whether surface is fouled, whether analyte is adsorbed or whether electron transfer slowed down at some point.
Curvature (second derivative) reveals how sharp or broad the peak is, if the peak is splitting, changes in mechanism and the instability in electron transfer rate.
The shape near the peak reveals charge transfer coefficient, reversibility, diffusion layer formation, capacitive versus faradaic formation.
Changes in baseline shape reveal electrode roughness, double layer capacitance, scan rate dependent behavior and contamination.
The multi dimensional patterns reveal micro-patterns, correlation between parts of graph, symmetry patterns, small drifts and frequency-like features.

V. Implementation and Coding Result:

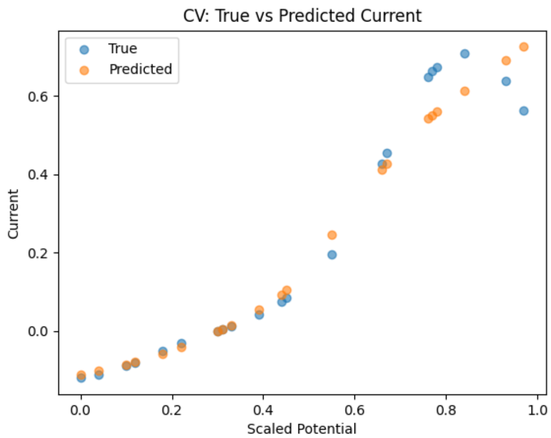

Figure 1: Forward Scan

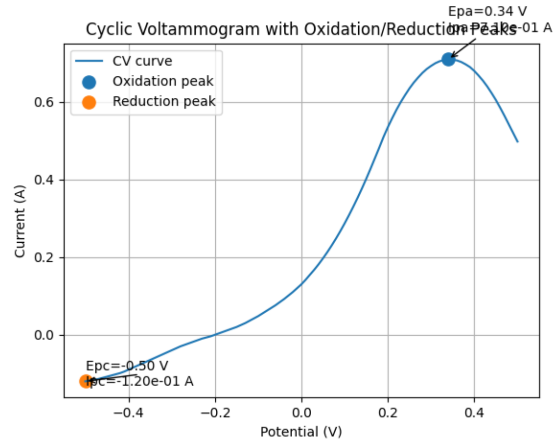

Figure 2: Oxidation Peak

Figure 1 represents the forward scan of the CA-125 sample used with the cyclic voltmmogram device. During this scan the potential or voltage is increased progressively to detect the increase in current. The analyte concentration strongly influences the forward scan. These characteristics make the forward scan particularly suitable for training machine learning models.

Figure 2 illustrates the oxidation peak observed during the forward scan of cyclic voltammetry. This peak displays the maximum electron transfer between the electrodes. Changes in peak height, width and curve dimensions records the overall understanding using this machine learning method. While traditional electrochemical methods primarily rely on this peak for quantification, in this work it is considered as one component within a broader set of curve-derived features used for machine learning analysis.

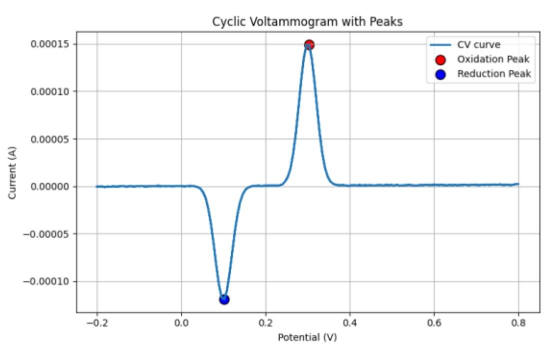

Figure 3: Oxidation and Reduction Peak

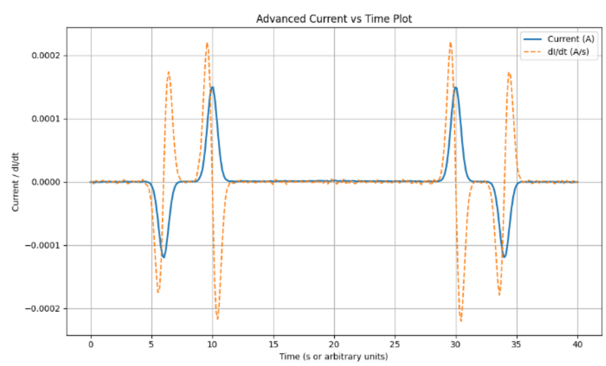

Figure 4: Current versus time

Figure 3 shows both oxidation and reduction peaks obtained from a complete cyclic voltammetry cycle. The oxidation peak arises during the forward sweep, while the reduction peak appears during the reverse sweep of the applied potential. However, due to the reverse scan having minor differences or changes during its scan, the forward scan is only considered for our analysis.

Figure 4 presents the current response of the electrochemical sensor as a function of time during the detection process. The current–time behavior provides discrete data to voltage respected measurements and is useful for understanding reaction stability, and transient effects. Such time-domain characteristics can enhance analytical interpretation and support advanced detection by data driven process.

VI. Conclusion: This paper presented an integrated approach for the early-stage detection of cancer biomarkers, with a primary focus on CA-125, using a paper-based microfluidic electrochemical sensing platform combined with advanced machine learning techniques. The use of the cyclic voltammogram was used in extracting the forward scan and feeding it to the machine learning algorithm.

By treating the cyclic voltammogram curve and extracting the high-dimensional data it was approved that this provided a detailed interview of the characteristics of the reaction taking place at the electrode. The proposed ML-based framework is capable of extracting hidden patterns related to reaction dynamics and fundamental data of the process.

The proposed micro fluidic platform proceeds with low cost, multiplexed and ready to use device which can detect the four analytes given the boost with the machine learning algorithms. The integration nanomaterial integrated electrodes enhanced the reaction mechanism, lowers limit of detection and helps in the overall efficiency of the entire reaction.

Overall, this is a cancer antigen detection integrated with machine learning application. This introduces an advanced ingredient for cyclic voltammogram detection methodology.

In the future work work will be forwarded in exploring better accurate and robust machine learning algorithms paving the way of this conference paper into a high quality journal paper with actual experimentation.

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