Applications of electrochemical sensors in the monitoring of chemical species in the environment: an analysis of impact

JUAN C.M. GAMBOA[1].

1. *Universidad de Tarapacá EIEE, Avenida 18 Septiembre #2222, Arica, Chile.*

ABSTRACT

In recent years, electrochemical sensors have garnered significant attention in the environmental field due to their potential to offer effective solutions for addressing the environmental challenges our planet faces, particularly in proactive environmental preservation. A particular interest has been focused on the development of electrochemical sensors due to their restricted sample volume and the potential for system miniaturization, enabling portability. Taking these aspects into consideration, this review centers on the utilization of electrochemical electrodes to acquire relevant chemical information pertaining to environmental issues. Furthermore, it will analyze how the use of nanotechnology has provided new substrate alternatives for the determination of chemically significant species in the environment. Finally, the challenges and future prospects in this field are discussed.
Key words: *Electrochemistry; Sensors; Nanotechnology; Screen printed electrodes; environment.*

INTRODUCTION

Electrochemical sensors play a crucial role in the precise quantification of chemical species, making it easier to understand and address the challenges of pollution and environmental degradation in our surroundings [1-3]. In recent years, there has been a surge in the production and use of chemicals across industries, leading to widespread environmental contamination that significantly impacts human health. Consequently, researchers have turned to electrochemical sensors to quantify chemical elements and assess their impact on the environment.

The rapid measurement, selectivity, sensitivity, low-cost analysis, minimal waste in the analysis process, and portability of these sensors are vital for real-time decision-making [4-8]. Furthermore, electrochemical techniques stand out for their versatility, allowing control of electronic reactions by modifying the electrode's surface and dynamically adjusting the applied potential to the solution [9-13]. This approach aims to eliminate potential interferents and achieve high sensor selectivity.

This article focuses on reviewing recent advances in electrochemical sensors and their impact on quantifying environmental species.

Principles of Electrochemical Sensors

Electrochemical sensors are built upon the principles of electrochemistry, a branch of chemistry that studies chemical reactions involving electron transfer and the conversion between chemical and electrical energy. These sensors leverage the interaction between chemical components and electric current to detect and quantify chemical species in liquid or gaseous samples. They consist of three essential components: the working electrode, reference electrode, and auxiliary electrode (Figure 1).

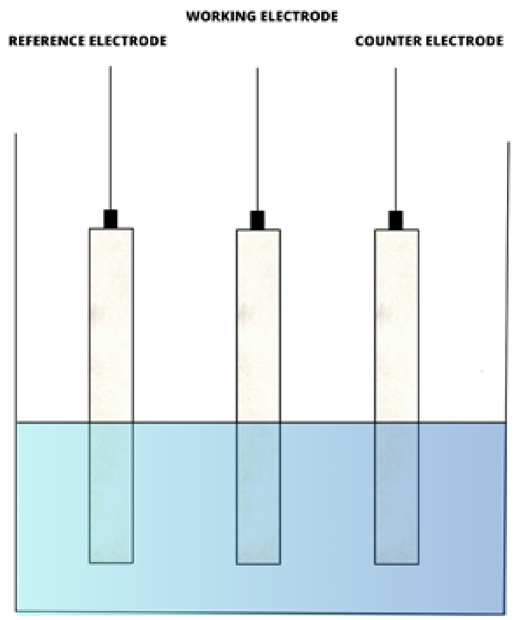
The working electrode is the central component of the electrochemical sensor and directly contacts the sample being analyzed. Typically, it's made from a conductive material such as gold, platinum, or modified glassy carbon. The surface of the working electrode is where the electrochemical reaction of interest takes place, which may involve electron transfer between the electrode and chemical species in the sample.

The reference electrode establishes a constant potential against which the potential difference at the working electrode is measured. This provides a stable reference for electrochemical measurements. The most commonly used reference electrode is the saturated calomel electrode (SCE), although other types like the silver/silver chloride electrode (Ag/AgCl) also exist.

The auxiliary electrode, also known as the counter electrode, offers an additional pathway for the electric current flow and maintains charge neutrality in the electrochemical cell. This electrode is not directly involved in the reaction of interest and is typically made from an inert conductive material like platinum. Electrochemical sensors operate through various mechanisms, including Voltammetry, Amperometry, and Electrochemical Impedance Spectroscopy. Each one of them will be discussed in detail below.

***Author for correspondence:** *dr.jcmgamboa@gmail.com*

Figure 1. Electrochemical Cell.



Voltammetry is an electrochemical technique that provides quantitative and qualitative information based on a current-voltage curve recorded using a potentiostat on a set of electrodes immersed in a solution.

The resulting curve is called a voltammogram, and the current flowing in the circuit depends on the oxidation or reduction of an electroactive species at the electrode-solution interface. This technique enables the identification of chemical species and their concentrations [14-16]. There are several variations of Voltammetry, each exploring different aspects of electrochemical reactions:

Cyclic Voltammetry (CV)
In this mode, the electrode's potential is cyclically varied between two extreme values. The resulting current is recorded as the potential changes, generating a characteristic "voltammogram" that provides information about current peaks corresponding to specific redox processes. CV is useful for identifying chemical species and evaluating reaction reversibility.

Differential Pulse Voltammetry (DPV)
In this technique, a small potential pulse is applied to the working electrode while measuring the current. The current is then recorded upon returning to the initial potential. The difference between these two currents provides information about the redox reaction of interest, enabling the identification and quantification of analytes.

Square Wave Voltammetry (SWV)
In this mode, the potential changes in a square wave pattern with abrupt shifts between two potential levels. The current is recorded during potential variation and analyzed to obtain information about electroactive species in the solution.

Pulse Voltammetry
This technique applies potential pulses to the working electrode instead of continuously changing the potential. This allows a more precise control of electrochemical conditions and can improve the resolution in the detection of chemical species.
Voltammetry has a wide range of applications in fields such as analytical chemistry, environmental research, and monitoring of chemical species in biological systems [17,18]. The sensitivity and selectivity of voltammetry can be improved by modifying electrodes, using molecular recognition techniques, and combining with other analytical techniques.

Amperometry is a powerful and versatile electrochemical technique used to measure the electric current generated by a redox reaction at a working electrode. This technique provides quantitative information about the concentration of chemical species present in a solution, making it an essential tool in a wide range of fields, from chemical analysis, biological analysis, and environmental monitoring [19]. It is based on Faraday's Law, which states that the amount of charge transferred in a redox reaction is proportional to the amount of substance participating in the reaction. By applying an appropriate potential to the working electrode, electrons flow between the electrode and the species in the solution, generating an electric current that is measured and interpreted to determine the analyte's concentration [19].

In environmental monitoring, amperometry plays a crucial role by allowing real-time detection of chemical contaminants in the air [20], water [21], and soil [22]. Its ability to perform in-situ and real-time measurements facilitates early threat identification and informed decision-making for environmental management and protection.

Electrochemical Impedance Spectroscopy measures the frequency response of an electrochemical system subjected to an alternating current or potential signal. This technique determines the resistance of the electrode/solution interface, providing information about the concentration and interaction of chemical species in the sample. In an environmental context, impedance is used to study and analyze the response of natural systems to electrical or electromagnetic signals. Applications include soil characterization for moisture content evaluation [23], detection of contaminants in groundwater [24], and monitoring plant health through electrical measurements [25]. These techniques provide valuable information about soil quality, pollution, and ecosystem health.

Electrochemical Sensors
Electrochemical sensors are devices that convert a specific electroactive species' chemical or physical property into a measurable signal (current), with its magnitude typically proportional to the analyte's concentration [26]. These sensors take advantage of the relationship between electric current and analyte's concentration at an electrode-solution interface.
An essential part of electrochemical sensors is the modification of the electrode's surface, which involves deliberately altering

the composition or structure of its superficial layer to improve sensitivity, selectivity, and stability. By modifying the surface, it is possible to optimize the interaction between the analyte and the electrode, leading to a higher electrical response for lower concentrations of analyte. Additionally, modification can help reduce interference from other substances present in the sample, thus improving the sensor's selectivity.

The modification of the electrode's surface is crucial because it can significantly influence the effectiveness and accuracy of electrochemical detection. Some of the most common electrode modification techniques include:

Coatings

Application of thin layers of specific materials onto the electrode to enhance selectivity and sensitivity. These coatings can be designed to selectively interact with the target analyte or to increase electrochemical charge transfer. Researchers [27-31] modify a glassy carbon electrode with thin films of bismuth or mercury in order to quantify heavy metals.

Nanomaterials

Incorporation of nanomaterials such as metallic nanoparticles, carbon nanotubes, or nanocomposites onto the electrode's surface. These nanomaterials can increase the electrode's effective surface area, improve charge transfer, and enable a more sensitive detection. J.C.M. Gamboa [32], uses a modification of carbon nanotubes and gold nanoparticles for the determination of Arsenic (III) in real samples. G. Lui [33] explores the use of carbon nanotubes in the fabrication of electrochemical sensors. Carbon nanotubes are used to enhance the sensitivity and selectivity of the sensors, making them suitable for the detection of analytes in environmental samples.

Biomolecules

Immobilization of biomolecules such as enzymes, antibodies, or nucleic acids to modify the electrode's surface. These biomolecules can specifically recognize and react with the analyte, allowing selective detection and the creation of biosensors. Sánchez [34] addresses the use of metal-organic frameworks in electrochemical detection platforms for environmental monitoring. These structures provide highly porous and selective surfaces for the detection of analytes in environmental samples.

Rahman [35] highlights recent advances in electrochemical sensors and biosensors for monitoring environmental pollutants. It examines various strategies and technologies used to improve the detection and quantification of contaminants in the environment. J. Wang [36], although focusing on medical applications, emphasizes the importance of electrochemical biosensors in disease detection and how their principles could be similarly applied in environmental monitoring.

NANOTECHNOLOGY IN ELECTROCHEMICAL SENSORS

The convergence of nanotechnology and electrochemistry has generated a paradigm shift in the development of sensors for environmental applications. The manipulation and control of materials at the nanoscale have opened new possibilities for enhancing the sensitivity, selectivity, and efficiency of electrochemical sensors, enabling a more effective approach to environmental challenges. Below, the impact and implications of nanotechnology will be examined in the field of electrochemical sensors for environmental applications.

Improvement of Sensitivity and Selectivity

Nanotechnology has enabled the creation of nanostructured and nanocomposite materials that exhibit unique properties. These materials can be functionalized to selectively interact with specific compounds, thereby increasing the sensitivity and selectivity of sensors. The presence of nanomaterials such as carbon nanotubes, metallic nanoparticles, and nanowires on electrodes' surfaces allows for a larger surface area and a more efficient interaction with analytes, resulting in enhanced detection and quantification of contaminants.

Miniaturization and Portability

Nanotechnology has enabled the miniaturization of essential components of electrochemical sensors. The creation of nanostructured electrodes and miniature detection systems has led to smaller and more portable sensors. This miniaturization is particularly valuable for implementation in in-situ and real-time monitoring systems in hard-to-reach locations.

Expanding Detection Range

Nanotechnology has provided tools to expand the detection range of electrochemical sensors. Surface modification with nanomaterials can improve the detection of compounds that were previously not easily detectable. The expansion of the detection range is essential for addressing the detection of emerging contaminants and low-concentration compounds in the environment.

Improving Kinetic Response

The kinetics of electrochemical reactions can be a limiting factor in detection. Nanotechnology has allowed for the acceleration of these reactions by providing a larger surface area and reducing the diffusion distances of analytes. This results in an improvement in the response speed of sensors, enabling faster and more accurate measurements.

An example of the advantages described is the research developed by J.C.M. Gamboa, "Screen Printed electrode of carbon nanotubes modified with Gold nanoparticles for simultaneous determination of Zinc, Lead, and Copper" [37]. This work presents an investigation on the development of a screen-printed electrode modified with carbon nanotubes and gold nanoparticles for the simultaneous detection of zinc, lead, and copper in aqueous solutions. The main objective is to improve the sensitivity and selectivity of the sensor for the measurement of heavy metals, which are environmental contaminants of concern. The screen-printed electrode is modified with carbon nanotubes, which provide a larger surface area and adsorption capacity for the metals studied. Additionally, gold nanoparticles are deposited onto the carbon nanotubes to further enhance the detection capability and selectivity.

The results show that the modified electrode exhibits improved electrochemical response for the simultaneous detection of zinc, lead, and copper in aqueous solutions. The proposed technique allows for measurement on a single electrode, simplifying the process and reducing the need for multiple analyses.

Consequently, this work demonstrates the feasibility of using a screen-printed electrode modified with carbon nanotubes and gold nanoparticles for the simultaneous detection of heavy metals in aqueous solutions. This research has significant implications for environmental monitoring and real-time pollutant detection, contributing to the protection and preservation of the environment.

In conclusion, the incorporation of nanotechnology into electrochemical sensors has transformed the way environmental challenges are assessed and addressed. The ability to manipulate and design materials at the nanoscale has allowed for significant improvements in the sensitivity, selectivity, speed, and portability of sensors. As research continues to advance, nanotechnology is expected to play a fundamental role in creating more efficient and versatile electrochemical sensors for the protection and preservation of the environment.

Environmental Impact and Benefits. In the constant pursuit of effective solutions to address the environmental challenges our planet faces, electrochemical sensors have emerged as a fundamental tool with a significant impact on environmental preservation. These innovative devices have revolutionized how we monitor and assess the quality of our surroundings, providing a clearer understanding of the effects of human activities on nature and offering substantial advantages for environmental management and mitigation of issues.

One of the most notable features of electrochemical sensors is their ability to accurately detect and quantify a wide variety of chemical compounds present in different environmental matrices, such as air, water, and soil. This highly specialized analytical capability allows for the early identification of contaminants and toxic substances, which is essential for air quality assessment, monitoring the health of water bodies, and detecting potential risks to human health.

The benefits of electrochemical sensors extend beyond their detection accuracy. These devices are also recognized for their speed and efficiency in generating data. By providing real-time measurements, they enable an immediate response to critical environmental situations, such as chemical spills or emissions of pollutant gasses. This rapid responsiveness is crucial for minimizing exposure to environmental hazards and reducing potential negative impacts on public health.

The versatility of electrochemical sensors is another key aspect contributing to their positive impact on the environment. These devices are applicable in a variety of contexts, from monitoring water quality in rivers and lakes to assessing air pollution in urban areas and detecting heavy metals in agricultural soils. This adaptability makes them an essential tool for scientific research, long-term monitoring, and the implementation of environmental policies and regulations.

Additionally, electrochemical sensors excel in their contribution to environmental sustainability. Through their ability to provide on-site and real-time measurements, these devices reduce the need for manual sampling and laboratory analysis, thereby decreasing resource consumption and waste generation associated with traditional methods. This efficiency has a positive impact on reducing environmental footprint and enhances data-driven decision-making.

Challenges and Future Directions. Despite their benefits and significant advancements, the implementation of electrochemical sensors for assessing en-vironmental impact does have some technical, operational, and economic challenges. However, these challenges also highlight the areas where research and innovation remain crucial to maximize the potential of electrochemical sensors in environmental preservation. Below are some key challenges and future directions in this field:

Calibration and Standardization. Calibration and standardization are critical aspects in the successful application of electrochemical sensors for assessing environmental impact. These processes directly influence the accuracy, reliability, and comparability of measurements made by the sensors, which in turn have a significant impact on the quality of collected data and informed decision-making. Establishing reliable standards and calibration methods is essential to ensure accurate and comparable measurements in different environments.

Selectivity and Specificity. Selectivity and specificity of electrochemical sensors can often be a challenge, especially in complex environments where multiple chemical compounds may be present. Improving selectivity to detect a specific target while minimizing interference from other compounds is a critical research direction to ensure reliable and accurate measurements.

Miniaturization and Portability. While there have been significant advancements in the mi-niaturization of electrochemical sensors, creating highly portable and cost-effective devices remains an important goal. The ability to bring detection technology to remote or hard-to-reach areas would facilitate broader and extensive environmental monitoring for real-time measurements.

Durability and Maintenance. Electrochemical sensors are often exposed to adverse envi-ronmental conditions, which can affect their durability and long-term performance. Research in durable materials and effective maintenance strategies is essential to ensure sensors function reliably over extended periods.

Data Integration and Platforms. Collecting and managing data generated by electrochemical sensors can be a challenge in itself. Data integration into accessible platforms and effective interpretation of results are areas that require further development to turn information into actionable insights. A good initiative should be directed towards developing integrations with small devices like tablets or smartphones to enhance portability.

Development of New Applications. As electrochemical sensor technology evolves, new possibilities for environmental applications arise. Exploring and developing sensors to detect emerging compounds, assessing soil quality more accurately, or measuring specific environmental parameters are promising research areas.

Therefore, electrochemical sensors present exciting opportunities to understand and address environmental impact. Although they face challenges in terms of calibration, selectivity, and miniaturization; research and innovation continue to be on the path to overcome these obstacles. The constant evolution of technology and collaboration among scientists, engineers, and decision-makers are essential to ensure that electrochemical sensors remain a valuable tool in environmental preservation and to build a more sustainable future.

CONCLUSIONS

In an increasingly environmentally conscious world, electrochemical sensors have emerged as a promising technology to address environmental challenges and improve the quality of our surroundings. These innovative devices play a crucial role by providing a precise and effective solution to monitor and understand the impact of human activity on nature.

One of the greatest benefits of electrochemical sensors lies in their ability to detect and quantify a wide range of chemical compounds in diverse environments, such as air, water, and soil. They enable early and accurate detection of contaminants and toxic substances, which in turn facilitates informed decision-making in environmental management and the implementation of mitigation strategies.

In addition to their detection accuracy, electrochemical sensors offer a significant advantage in terms of time and efficiency. Their ability to provide real-time measurements allows for a rapid response to emergency situations, such as chemical spills or the release of toxic gases. This helps minimize environmental damage and protect public health by providing immediate and reliable data. Another important aspect is the versatility of electrochemical sensors in various environmental applications. From monitoring water quality in rivers and lakes to detecting atmospheric pollutants in urban areas, these devices adapt to a variety of contexts and needs. Their ability to operate in different matrices and climatic conditions makes them a valuable tool in research and long-term monitoring.

Additionally, electrochemical sensors contribute to environmental sustainability by reducing the need for manual sampling and time-consuming laboratory analysis. This decreases the environmental impact associated with traditional procedures and provides decision-makers with more accurate data and opportunities to implement proactive solutions.

In this way, electrochemical sensors have a positive and significant environmental impact by providing a powerful tool for environmental monitoring and assessment. Their ability to rapidly, accurately, and in real-time detect contaminants, coupled with their versatility and efficiency, makes them key allies in the fight for a cleaner and more sustainable environment.

REFERENCES

1. J. Wang, *Analytical chemistry,* 78, 4005-4018, (2006).
2. G. Liu & Y. Lin, *Analytica chimica acta,* 683(1), 17-27, (2011).
3. S. Vaddiraju, I. Tomazos, D.J. Burgess, F. C. Jain, & F. Papadimitrakopoulos, *Biosensors and bioelectronics,* 25(7), 1553-1565, (2010).
4. J. Wang, *Biosensors and bioelectronics,* 21(10), 1887-1892, (2008).
5. T. Liao, J. Zhang, J. Li, & S. Zhang, *Sensors and Actuators B: Chemical,* 255(3), 3015-3021, (2018).
6. L. Lu, X. Xu, X. Zhang, X. He, L. Fu, L. Zhang, & C. Li, Sensors and Actuators B: Chemical, 286(1), 90-99, (2019).
7. Y. Zhang, S. Luo, X. Zu, X. Jiang, H. Zhu, & L. Mao, Biosensors and Bioelectronics, 91(1), 188-195, (2017).
8. Y. Wang, N. Xia, G. Wang, & C. Gong, Microchemical Journal, 156(1), 104740, (2020).
9. A. J. Bard & L. R. *Faulkner, Electrochemical methods: fundamentals and applications* (Vol. 2), John Wiley & Sons, 2001
10. 10. R. G. Compton, Electrochemistry, Oxford University Press, 2018
11. A. Ivaska & A. Lewenstam (Eds.), *Electrochemical sensors, biosensors, and their biomedical applications,* Elsevier, 2019.
12. O. K. Oyewole, J. M. Elliott, & R. H. Colby, *Chemical reviews,* 117(15), 10446-10519, (2017).
13. Y. Li & X. Huang, *Biosensors and Bioelectronics,* 150(1), 111895, (2020).
14. A.J. Bard, L.R. Faulkner, *Electrochemical methods: fundamentals and applications*, Vol. 2, John Wiley & Sons, 2001.
15. J. Wang, Analytical electrochemistry, John Wiley & Sons, 2006
16. C.M. Brett, A.M.O. Brett (Eds.), *Electroanalytical techniques, Springer Science & Business Media*, 2008.
17. R.G. Compton, C.E. Banks, *Understanding voltammetry, World Scientific,* 2010.

18. J. Wang, A. Merkoci (Eds.), Electrochemical nanosensors, *Springer Science & Business Media,* 2008.
19. P.T. Kissinger, W.R. Heineman, *Laboratory techniques in electroanalytical chemistry* (2nd ed.), CRC Press, 1996
20. J. Rubio, H. Aguilar, J.A. Hernan, F.J. Ávila-Camacho, J.M. Stein-Carrillo, A. Meléndez-Ramírez, *Ingeniería Investigación y Tecnología,* 2, 211-222, (2016).
21. G. Marrazza, I. Chianella, M. Mascini, *Environmental Biosensors,* Springer, 2011.
22. Q. Hu, D.-X. Liu , *InTech,* 2015.
23. D.A. Robinson, S.B. Jones, I. Lebron, H. Vereecken, *Vadose Zone Journal,* 8, 829-843, (2009).
24. B. Adhikari, P.P. Adhikary, R. Hernandez, *Environmental Science and Pollution Research,* 22, 10931-10941, (2015).
25. Y. Alkhazneh, H.R. Bozorgi, G. Kroumpouzos, Biosystems Engineering, 96, 126-142, (2020).
26. J. and D. Xu, *Analytica Chimica Acta,* 998, 1-17, (2017).
27. X. Liu, J. Li, Electroanalysis, 15, 21, 1775-1780, (2003).
28. X. Liu, J. Li, Analyst, 129, 576, (2004).
29. J. Wang, J. Lu, *Electrochemistry Communications,* 5, 1026, (2003).
30. T. Gan, P. Singh, Y. Liu, M. Li, *Electroanalysis,* 29, 1089, (2017).
31. R. Venu, M. Ramakrishna, G. Madhavi, Analytica Chimica Acta, 912, 1, (2016).
32. J.C.M. Gamboa, L. Cornejo, J.A. Squella, *Journal of Applied Electrochemistry,* 44, 1593, (2014).
33. G. Liu, Y. Lin, *Electroanalysis,* 18, 319, (2006).
34. E. Sánchez-Tirado, L. Agüí, D. Pérez-Quintanilla, *TrAC Trends in Analytical Chemistry,* 115, 28, (2019).
35. M. A. Rahman, P. Kumar, K. H. Kim, Journal of Hazardous Materials, 347, 194, (2018).
36. J. Wang, Biosensors and Bioelectronics, 21, 1887, (2006).
37. J. C.M.Gamboa, Chil. Chem. Soc., 65, 2, (2020).