Application of Electrochemical Detection Technology in Environmental Pollutant Monitoring

Wenhan Lu[1,a], Xiang Zhang[2,b*]

[a]529324426@qq.com, [b]*70964060@qq.com

[1]Jiangsu Shang Weiss Environment Technology Co.td, Nantong, 226000, PR China
[2]Nantong Ecological Environment Monitoring Center, Nantong, 226000, PR China

Abstract: Electrochemical detection technology is an emerging technology in the field of modern environmental pollutant and environmental microdetection technology. This paper analyzes the key technologies of electrochemical detection and explores its specific applications in the detection of typical environmental pollutants and water quality analysis from three aspects: aquatic, atmospheric, and soil environments. The aim is to provide a reference for improving the technical level of environmental monitoring.

Keywords: Electrochemical Detection; Environmental Pollutants; Application

1 Introduction

With the development of society and the economy, an increasing number of pollutants are being introduced into the environment, posing catastrophic disasters to human development and the entire global ecosystem. The types of pollutants in the environment are numerous, with heavy metals and persistent organic pollutants being particularly harmful. Therefore, there is an urgent need for methods that can quickly and accurately perform qualitative or quantitative analysis of these pollutants on-site. Currently, there are various methods for detecting environmental pollutants, such as gas chromatography, fluorescence analysis, high-performance liquid chromatography, and chromatography-mass spectrometry. These methods involve expensive equipment and require cumbersome sample pre-treatment, are time-consuming, and costly. Electrochemical sensors, on the other hand, have attracted considerable attention due to their low detection limits, high stability, miniaturization, intelligence, and simple operation. They have been widely researched and applied in many fields, including food safety, industrial production, healthcare, and environmental protection.

2 Key Technologies in Electrochemical Detection

2.1 Electrochemical Sensor Technology

Electrochemical sensors are a type of chemical sensor and represent a special class of sensors in modern chemical analysis. They primarily capitalize on the electrochemical reactions of pollutants occurring at the electrode surface. Subsequently, this sensory information is converted into recognizable electrical signals through specific transducers, enabling

IDEE 2023, November 24-26, Zhengzhou, People's Republic of China

DOI 10.4108/eai.24-11-2023.2343445

identification. This conversion enables the qualitative or quantitative analysis of the target substances using the instrument [1], as shown in Figure 1.

Figure 1 Electrochemical Sensor

The working principle of the electrochemical sensor is illustrated in Figure 2: initially, the target analyte diffuses to the surface of a specific working electrode, where an electrochemical reaction occurs. The electrochemical signals generated undergo conversion by a signal transduction element, transforming into voltage, current, conductivity, or other identifiable electrical signals. Subsequently, the electrochemical detection instrument amplifies and processes the signals. Finally, the processed signals are transmitted to a computer for output display, completing the entire detection process of the target analyte content in the sample.

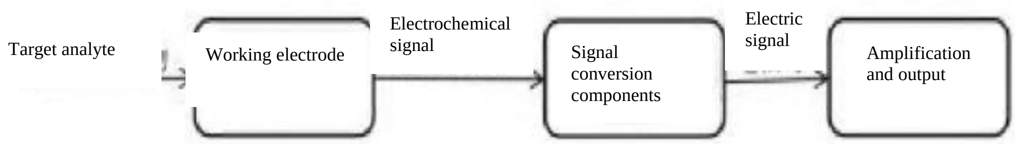

Figure 2 Working Principle of an Electrochemical Sensor

2.2 Preparation of Electrochemical Sensors

Various methods for detecting heavy metal ions include spectrophotometry, mass spectrometry, and electrochemical methods. Due to their simplicity, low cost, and ease of operation, electrochemical methods play a significant role in the field of heavy metal ion detection. Chen Chen et al. from East China University of Science and Technology [2] prepared porous screen-printed carbon electrodes using screen printing technology combined with template synthesis. They modified these electrodes with a bismuth film, enabling the detection of lead and cadmium ions with detection limits reaching 0.03 µg/L and 0.34 µg/L, respectively. The coating method involves dispersing pre-prepared metal ion-imprinted polymer particles in an organic solvent. The mixed solution is then applied to the electrode surface through methods such as drop coating, spin coating, and dip coating. Finally, the solvent is evaporated to obtain the desired ion-imprinted modified electrode. Wang Zhiqiang et al. from China Agricultural University [3] used conductive material molecular wires as binders to create a novel carbon paste electrode. This electrode was further modified with a Nafion film and a tin film on its surface. Using this electrode, they measured cadmium ions in multiple samples of agricultural irrigation water, achieving a detection limit of 0.13 µg/L. The results were compared with those obtained from atomic absorption spectrometry, and analysis showed that the electrochemical sensor had good detection accuracy and reliability. Zou Shaofang et al. researched the application of electrochemical sensors in the detection of heavy metals in seawater and developed an integrated microsensor for multi-element heavy metal detection. This sensor is primarily used to measure the content of various elements like zinc, copper, manganese, arsenic, iron, and chromium. Lau et al. studied an electrochemical sensor capable of simultaneously detecting Pb2+ and Cd2+ using the heavy metal ion imprinting technique. This sensor was designed based on the principle of a light-emitting diode (LED), and the detection limits for both metal ions could reach the nmol/L range.

2.3 Prospects for the Application of Electrochemical Sensors

(1) Application of TiO2 Nanotubes in Gas Sensors

Starting with Varghese et al. initial proposal for an H2-sensitive TiO2 nanotube gas sensor, there has been gradual development and improvement in preparing sensors that can operate at room temperature. Subsequently, Ma Shicai employed an electrochemical anodization method to develop a TiO2 nanotube gas sensor sensitive to methanol. Further research has produced Ti02 nanotube sensors sensitive to gases like nitrogen dioxide, carbon monoxide, hydrogen, ethanol, and toluene [4].

(2) DNA Electrochemical Sensors Modified with Multi-walled Carbon Nanotubes (MWCNT)

High-sensitivity DNA electrochemical sensors have been fabricated based on the DNA/ZrO_2/MWCNT/GCE structure, where a porous zirconia film is deposited on a glassy carbon electrode modified with multi-walled carbon nanotubes (MWCNT/GCE) at room temperature using electrochemical detection methods. The large specific surface area of MWCNTs, their excellent electron transfer properties, the biocompatibility of zirconia, and the strong adsorption capacity for DNA significantly enhance the immobilization of DNA probes and the sensitivity of DNA hybridization detection [5].

(3) Gold Nanoparticle Electrochemical Sensors

A typical gold nanoparticle electrochemical sensor consists of a cathode (detection electrode) and an anode, with the electrodes modified by gold nanoparticles and separated by a thin layer of electrolyte. The advantages of gold nanoparticle electrochemical sensors include short response times, high sensitivity, selectivity, and wide application in measuring concentrations in gases and liquids, as well as in biosensing. The advantages and disadvantages of electrochemical sensors are summarized in Table 1.

Table 1 Advantages and Disadvantages of Electrochemical Sensors

	Advantages	Disadvantages
1	Capable of detecting specific environmental pollutants.	Limited temperature range.
2	Linear output, low power consumption, and good	Short lifespan.

	resolution.	
3	Good repeatability and accuracy.	High cross-sensitivity with other gases.
4	Not contaminated by other gases. The presence of other environmental gases does not shorten the sensor's lifespan.	The longer the exposure to the target gas, the shorter the lifespan.
5	Low cost, reasonable structure, simple device, and convenient operation.	

3 Specific Applications of Electrochemical Detection in Environmental Monitoring and Analysis

3.1 Application in Monitoring and Analysis of Water Environmental Pollutants

(1) Heavy Metal Detection

Heavy metals pose a significant threat to water environments and are one of the primary focuses of water environmental monitoring. For the detection of heavy metals in water environments, electrochemical detection techniques can be employed to determine the characteristics of heavy metals in the water. ① Gold electrodes modified with graphene nanomaterials can be used to detect hexavalent chromium (Cr(VI)) in water environments, offering a linear range of 5～2000μg/L and a detection limit of approximately 0.5μg/L. These electrodes exhibit good interference resistance against divalent ions such as magnesium, copper, and nickel. ② Anodic stripping voltammetry (ASV). Sensors installed on carbon material electrodes are utilized to detect divalent cadmium ions in water environments, with a linear range of 0.5～40μg/L and a detection limit of about 0.15μg/L; ③ Composite nanocarbon materials, serving as the electrode body, can detect divalent lead ions in water, with a detection limit as low as 3.8×10-12mol/L [6]. Lu Zhiwei et al. integrated the portability and disposability of screen-printed carbon electrodes (SPCE), the high conductivity of gold nanoparticles (AuNPs), and the exceptional electrocatalytic properties of bismuth (Bi) films. They have constructed a Bi/AuNPs/SPCE electrochemical sensor using an in-situ electrodeposition method.

(2) Inorganic Salts Detection

Water environments contain inorganic salts such as SO_3^{2-}, NO_2^-, BrO_3^-, etc. Electrochemical detection techniques can be applied for the detection of inorganic salts in water environments. ① Composite nanomaterials are used through chronoamperometry to detect SO_3^{2-} in water environments. The detection results indicate that the method has a relatively high sample recovery rate and a broad linear range, spanning from 3～1000μmol/L, with a detection limit of 1.6μmol/L; ② After modifying glassy carbon electrodes with bromophenol blue, the presence of NO_2^- in water environments can be detected. This method is used for the inorganic salt detection in lake water, with a linear range of 0.02-109.1 μmol/L and a detection limit of 5 μmol/L; ③ Capillary electrophoresis modified carbon disk electrodes are used to detect BrO_3^- in water environments. The results show that under optimal conditions, the detection method has a linear range from $5.0×10^{-8}$～$5.0×10^{-5}$mol/L, with a detection limit of $2.0×10^{-8}$mol/L[7].

(3) Organic Pollutant Detection

Considering the current situation of water environment pollution in China, the content of organic pollutants is showing an increasing trend. Therefore, accurate detection of organic pollutants is particularly necessary. Electrochemical detection techniques can be used to detect organic pollutants in water environments. ① After modifying glassy carbon electrodes with graphene, pentachlorophenol in water environments can be detected. This method has a linear detection range of 1.0×10-7-1.0×10-5mol/L and a detection limit of 2.3×10-8mol/L; ② Carbon paste electrodes modified with cetyltrimethylammonium bromide (CTAB) and montmorillonite can be used to detect phenol in water environments. This method performs well in wastewater detection, with a detection limit of 1.2×10-8 mol/L; ③ Cyclic voltammetry is used to determine polychlorinated biphenyls (PCBs) in water environments. This method is fast, with a linear range of 1.25～10μg/L[8].

3.2 Applications in Atmospheric Environment Monitoring and Analysis

In atmospheric environment monitoring, common pollutants include NO, SO2, CO2, TSP, etc. Traditional atmospheric monitoring methods typically use spectrophotometric techniques such as the saltzman method for NOx and the West-Gaeke method for SO2, which are operationally complex, costly, and inefficient. The application of electrochemical detection technology to atmospheric monitoring and analysis can overcome the shortcomings of traditional methods. ① An amperometric biosensor is constructed by immobilizing sulfite oxidase on an acetate fiber membrane and an oxygen electrode, which can complete the determination of SO2 samples within 10 minutes. When the concentration of sulfite is less than 3.4×10-4mol/L, the detection limit is 0.6×10-4mol/L; ② A biosensor is made by immobilizing a polymeric porphyrin nickel complex on a glassy carbon electrode, combined with flow injection analysis technology, which can be used to determine the content of SO2, with a detection limit of 0.15 mg/L; ③ A sensor is constructed by fixing a permeable membrane and nitrifying bacteria on an oxygen electrode, which can be used to determine the content of NO in the atmosphere, with a detection limit of 1×10-8mol/L[9].

3.3 Applications in Soil Environment Monitoring and Analysis

2.3.1 Pesticide Residue Detection

Pesticides play an important role in the production and storage of agricultural products and in the control of pests. Especially in countries with large populations and limited arable land, pesticides ensure high yields of crops, meeting the demand for agricultural products and creating significant economic benefits for humanity. However, the overuse of pesticides has led to environmental pollution and the presence of pesticide residues in agricultural products, posing serious health risks to humans. Xue Rui et al. used a graphene-Nafion composite as a solid-phase adsorbent to prepare an electrochemical sensor for the detection of organophosphorus pesticides; Zhang Weilong [10] et al. developed a novel electrochemical luminescence sensor functionalized with sodium polystyrene sulfonate graphene, which achieved the detection of three pesticides: imidacloprid, acetamiprid, and thiamethoxam, with detection limits of 0.667 ng/mL, 40 ng/mL, and 50 ng/mL, respectively.

2.3.2 Detection of Sulfides and Arsenic Compounds

Sulfides and arsenic compounds are serious pollutants in the soil environment. Traditional detection methods include iodometric titration and methylene blue colorimetry, but these methods require sample pre-treatment and often involve large measurement errors, making it difficult to meet the requirements for efficient determination. The application of electrochemical biosensors to the determination of sulfides and arsenic compounds can overcome the limitations of traditional methods. ① Thiobacillus, a sulfur-oxidizing bacteria, can be isolated from acidic soil and used as a molecular recognition element for a microbial electrode to determine sulfides. When the electrode is inserted into a buffer solution containing S^{2-}, the S^{2-} diffuses into the microbial film and is assimilated by the bacteria, causing a decrease in the electrode's output current. The change in current is recorded to accurately determine the concentration of sulfides; ② Green fluorescent protein extracted from seawater can be used to create a biosensor through genetic engineering techniques, which can detect trace amounts of arsenates and arsenites in soil. Electrochemical gas sensors primarily monitor the concentration and composition of gases by observing changes in current. Jian Jiawen et al. [11] used platinum electrodes and YSZ (yttria-stabilized zirconia) as an oxygen ion converter, which can detect NO in the range of $1X10^{-4}$μmol/L4-$1X10^{-3}$μmol/L. Moon et al. used tungsten oxide (WO_3) nanoparticles for the detection of NO_2, achieving a detection limit of 800 ppb, which meets the requirements for atmospheric monitoring.Conclusion

4 Conclusion

In summary, with the continuous progress and development of science and technology, electrochemical detection methods are also constantly being optimized and improved. Research in various aspects, such as electrochemical sensing technology, preparation of electrochemical sensors, and the application prospects of electrochemical sensors, has been widely promoted and has shown significant effectiveness. Against the backdrop of today's technological advancements, electrochemical analysis holds a very broad range of application prospects. Building upon this foundation, there is a need to develop environmentally monitoring devices that are highly sensitive and efficient. Furthermore, the direction of development should move towards automation and integration, laying a solid foundation for the improvement of environmental detection efficiency.

References

[1] Mo Li. Electrochemistry at the liquid interface and its application in environmental monitoring and analysis [J]. Heilongjiang Environmental Journal, 2014(4): 56-59.

[2] Liu Chunxiu, Ji Diansheng, Wu Yuanyuan. Analysis of the application of electrochemical sensing technology in marine environmental monitoring [J]Petrochemical Industry Technology, 2016(7): 202-202.

[3] Zhang Jian. Application of electrochemical sensors in environmental detection [J]. Energy Conservation, 2019(2): 91-92.

[4] Zheng Delun, Zhang Ruilong, Chen Jinlong. Research progress of electrochemical biosensors in environmental monitoring [J]. Guangdong Chemical Industry, 2015(17): 131-132.

[5] H. Razmi , H. Heidari. Amperometric determination of hydrogen peroxide on surface of a novel PbPCNF-modified carbon-ceramic electrode in acidic medium[J]. Journal of Electroanalytical Chemistry 625 (2009) 101–108
[6] C.Matsubara,N.Kawamoto,K.Takamala,Oxo[5,10,15,20-tetra(4-pyridyl)porphyrinato].titanium(IV): an ultrahigh-sensitive spectrophotometric reagent for hydrogen peroxide[J]. Analyst 117 (1992) 1781–1784
[7] Lin Xiaoer. Analysis of water quality detection system based on electrochemical detection methods [J]. Instrumentation, Analysis and Monitoring, 2020(03): 29-32.
[8] Deng Lu. Study on PEDOT-based ternary composite materials in electrochemical sensing for food quality and safety [D]. Jiangxi Science & Technology Normal University, 2022.
[9] A. Lobnik, M. Cajlakovic, Sol–gel-based optical sensor for continuous determination of dissolved hydrogen peroxide[J]. Sens. Actuators B: Chem. 74 (2001)194–199
[10] Z. Genfa, P.K. Dasgupta,W.S. Edgemond, J.N. Marx, Determination of hydrogen peroxide by photo-induced fluorogenic reactions[J]. Anal. Chim. Acta 243 (1991)207–216
[11] Ye Hongchun. Construction of new electrochemical sensors and their application in environmental detection [J]. Science and Innovation, 2016, 15(17): 91.