



Review Review of Underwater In Situ Voltammetry Analyzers for Trace Metals

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Abstract: This review is a comprehensive overview of recent advancements in underwater in situ heavy metal voltammetric analyzers (UIHVAs). It explores various types of in situ voltammetric analyzers, including the voltammetric in situ profiling system, submersible integrated multi-channel trace metal sensing probes, vibrating gold microwire electrode voltammetric analyzers, and electrochemical analyzers designed for on-site flow measurements. It also covers electrochemical sensors based on flexible liquid crystal polymers, deep-sea mercury sensors, and other in situ electrochemical analyzers. This review systematically examines the research and development progress of microelectrode arrays, screen-printed, carbon, bismuth, antimony, and lab-on-a-chip electrodes. The final section looks at key trends in the research and development of voltammetric analyzers, highlighting the exploration of novel working electrodes, the integration of smart monitoring and data analysis technologies, and the promotion of interdisciplinary collaboration and innovation. From a global perspective, in situ heavy metal voltammetric analysis technology has demonstrated significant applicability in various fields, such as environmental monitoring, marine science, and biogeochemistry. This technology holds considerable potential for further development. However, extensive research and continuous improvement are required to improve detection performance. We are convinced that with continued technological advances and dedicated research efforts, these challenges can be overcome and will pave the way for the widespread application of UIHVAs.

Keywords: underwater; in situ; voltammetry analyzer; trace metal

1. Introduction

The issue of heavy metal pollution in aquatic environments has become a significant global environmental concern [1–3]. Industrialization and urbanization have accelerated the discharge of heavy metal pollutants into water bodies through various pathways, including wastewater discharges, atmospheric deposition, and land-use change, significantly impacting water quality [4–7]. Heavy metals pose significant threats to ecosystems and human health due to their high toxicity, potential for bioaccumulation, and persistence in the environment [8–14].

Among the various techniques for detecting heavy metals, voltammetric analysis in electrochemistry has attracted significant attention due to its distinct advantages in analyzing heavy metal ions within complex matrices. This method enables high-precision in situ determination of heavy metals and allows for the simultaneous detection of multiple elements [15,16]. It offers rapid analysis, outstanding sensitivity and accuracy, good selectivity, minimal sample requirements, and a wide detection range. Additionally, its simplicity of operation and portability make it widely applicable in environmental monitoring and analysis [17].

Traditional heavy metal environmental monitoring primarily relies on centralized laboratory analysis, where samples are susceptible to various interferences during collection,



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Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). preservation, transportation, and processing, potentially affecting the accuracy of the results [18,19]. To more accurately reflect in situ heavy metal concentrations, the development of in situ heavy metal sensors is crucial. Underwater in situ voltammetric analyzers have emerged to address this need, inheriting the advantages of voltammetric analysis while offering real-time, continuous, and highly sensitive underwater in situ analysis capabilities [20,21]. Compared to traditional laboratory methods, this technology provides faster and more accurate data on the heavy metal content in water bodies [22,23].

Underwater in situ voltammetric analyzers achieve rapid and accurate detection of heavy metal ions by directly measuring their voltammetric characteristics underwater, demonstrating broad application prospects [24]. In the field of water environment monitoring, they can be utilized for real-time monitoring and assessment of heavy metal pollution in rivers, lakes, oceans, and other aquatic environments, aiding in the timely detection of, and response to, pollution issues. Additionally, in biological and oceanographic research, this technology provides an important means of monitoring heavy metal content in organisms, with profound implications for biogeochemical cycling studies [25–27]. However, the development of underwater in situ voltammetric analyzers faces numerous challenges, including the selection and design of electrode materials, optimization of signal acquisition and processing systems, and improvement of data transmission and storage technologies [28]. Future advancements in this technology will focus on enhancing detection sensitivity, reducing costs, simplifying operation processes, and meeting the needs of environmental protection and scientific research [29]. Meanwhile, ex situ electrochemical heavy metal detection techniques remain in a stage of continuous evolution and development. It is particularly noteworthy that the ongoing innovations in environmentally friendly electrode designs, including bismuth electrodes, antimony electrodes, and lab-on-a-chip systems, have infused new vitality into the field of heavy metal detection. When it comes to performing large-scale rapid measurement tasks, ex situ measurement techniques currently possess irreplaceable advantages due to their efficiency and convenience. With the continuous updating and improvement of technology, ex situ measurement will continue to play a significant role in the field of electrochemical heavy metal detection.

Recent advancements in the voltammetric analysis of heavy metals have demonstrated a significant increase in research output. This surge is evident in the number of publications indexed in the Web of Science over the past decade (2014–2024), where 2013 scientific articles include the keyword "Trace Metal, Voltammetric", and 276 of these also feature the keyword "in situ". This underscores the growing importance and research intensity surrounding in situ voltammetric analysis techniques. These studies encompass both fundamental theoretical research on heavy metal voltammetry and the practical application of this method in underwater in situ environments. Particularly in the domain of in situ detection technology, there is a focused effort on developing robust instruments capable of reliably performing heavy metal analysis in underwater settings. The advancement of such technologies holds substantial significance for environmental monitoring and marine ecological protection.

This review outlines the principles of in situ heavy metal voltammetric analysis technology, its main research directions, and the advantages of in situ measurements. It provides detailed introductions and comparisons of various in situ voltammetric analyzers, followed by a systematic analysis of electrode development. Finally, the paper examines the main development trends of current voltammetric analyzers, summarizing the research status, achievements, and existing challenges in this field (Figure 1). To date, only the voltammetric in situ profiling system has achieved commercial application in this field. Our review aims to provide a valuable reference for researchers by summarizing the current state of technology, highlighting the critical challenges, and offering insights into future research directions.



Figure 1. Instruments that have been developed include VIP/VGME/PG004. Advancements in electrode technology are of paramount importance for enhancing detection accuracy and efficiency. The main types of electrodes currently include microelectrode arrays, screen-printed, carbon, bismuth, antimony, and lab-on-a-chip electrodes.

2. Research Directions and Advantages of Voltammetry

Voltammetry is a pivotal technique for real-time, on-site, and in situ monitoring of trace metals, and there is increasing recognition of its importance in heavy metal ion analysis [30-34]. Research in this field is guided by the "6S" principle: Sensitivity, Selectivity, Size, Speed, Stability, and Safety [35]. Sensitivity, crucial for sensor performance, is enhanced by stripping voltammetry, which pre-concentrates target ions on the electrode surface, achieving detection levels in the parts-per-billion (ppb) range [36,37]. Advances focus on electrode modifications to improve electrochemical properties. Selectivity, essential for distinguishing different metal ions, is improved by modifying electrode surfaces with sensitive materials and using machine learning to analyze voltammograms [38]. Size affects instrument portability, with technologies like microelectrodes, screen-printed electrodes, and lab-on-a-chip enabling miniaturization and real-time field monitoring [39]. Speed, both an advantage and challenge, is advanced with techniques like Fast Scan Cyclic Voltammetry, although improvements in sensitivity and selectivity are needed [40]. Stability, challenged by natural water compositions, is maintained using disposable sensors and renewable surface electrodes [41]. Safety concerns over mercury electrodes have led to the development of mercury-free materials such as carbon, bismuth, and antimony, which enhance sensitivity and selectivity while meeting environmental standards.

Compared to traditional analytical methods, underwater in situ heavy metal voltammetry analyzers offer the following significant technical advantages.

Real-time monitoring enables immediate detection of heavy metals on-site, avoiding delays associated with laboratory analysis. This capability allows researchers to track dynamic fluctuations of heavy metals in water bodies accurately, providing a detailed understanding of pollutant dispersion patterns [42].

Portability is a major highlight; with compact and lightweight designs, these analyzers facilitate easy setup and use in various aquatic environments. This enhances the applicability

of the instrument in field studies, making it a powerful tool for environmental monitoring and scientific exploration [43].

Economic efficiency is achieved by reducing labor, material, and time costs, as sample transport and processing in the laboratory are eliminated. Additionally, this minimizes the risk of sample contamination during transit and storage [44].

3. In Situ Voltammetry Analyzer

3.1. From Voltage In Situ Profiling System to Submersible Integrated Multi-Channel Trace Metal Sensing Probe

In the 1990s, the Tercier-Waeber research group pioneered the development of on-chip micro-electrochemical sensors (GIMEs) [45], marking a significant advancement in electrochemical sensor technology. In 2005, these sensors, comprising an array of iridium-based microdisks coated with mercury film, were termed mercury film micro-electrochemical sensors (Hg-GIMEs) [46]. They enabled efficient in situ dynamic analysis of Cu(II), Pb(II), Cd(II), and Zn(II) at sub-nanomolar levels (2009, 2011, 2015). Subsequently, these Hg-GIMEs were integrated into the voltammetric in situ profiling (VIP) system, which demonstrated high-resolution in situ monitoring across various aquatic environments [47–49].

Recent advancements include the development of a new generation of GIME electrodes that further enhance sensing performance (2021). These electrodes employ more interconnected iridium-based microdisk arrays and utilize mercury or gold nanoparticles/filaments as the electrochemical coating, enhancing both sensitivity and detection range. Recent studies indicate that these new electrodes can accurately quantify inorganic arsenic (III) and mercury (II) in environmental samples with minimal pretreatment [50].

Creffield et al. (2023) effectively employed VIP systems with GIME electrodes to conduct in situ high-resolution quantification of the bioavailable nickel fraction in natural waters (Figure 2) [51].



Figure 2. Picture of the (**A**) in-house flowthrough plexiglass cell with the mini-electrodes (1, 2, and 3) and the shielded Plexiglas holder (4) enabling incorporation of the flowthrough cell into the bottom of the VIP electronic housing; (**B**) mini-reference electrode (1), the working microelectrode (2), and the mini-counter electrode (3); and (**C**) the VIP system made up of the peristaltic pump (1), the chirurgical bag containing the nioxime and buffer solutions (2), the voltammetric probe with the in-house flowthrough plexiglass cell at the bottom (3), and the chirurgical bag to collect the waste (4) [51].

The latest development from the Tercier-Waeber team, TracMetal (2021), is an advanced multichannel in situ electrochemical sensor. This compact, low-power sensor integrates the newly designed Hg-GIME and AuNF-GIME into a three-channel flow cell connected to a multichannel peristaltic pump, allowing for the automatic, real-time, simultaneous monitoring of multiple harmful metals in situ [52].

TracMetal has been successfully deployed for high-resolution monitoring in Arcachon Bay, an ecologically and economically significant area on the southwestern Atlantic coast of Europe. Comprehensive water sample analysis provides fundamental data on the dynamic concentrations and temporal variations of the bioavailable fractions of specific harmful metals, offering solid technical support for environmental impact studies (2021) [53,54]. However, the instrument's underwater in situ continuous operation duration has not exceeded 10 days, indicating a need for improved stability and reliability for long-term operation.

3.2. Vibrating Gold Microwire Electrode Voltammetric Analyzer

Gibbon-Walsh et al. (2011) introduced an electrochemical method for determining manganese and zinc concentrations in coastal waters using a vibrating gold microwire electrode (VGME) (Figure 3) [55]. Chapman et al. (2012) further explored the use of VGME by designing an apparatus for in situ copper monitoring in coastal waters [56]. Additionally, Domingos et al. (2016) applied VGME in the AGNES technique to quantify free copper concentrations directly [57]. This method facilitates metal detection in seawater without the need for reagents, making it ideal for in situ monitoring applications. The device integrates a VGME, an energy supply module, a potentiostat, and an advanced data acquisition system, enabling effective detection in areas up to 40 m deep.



Figure 3. Photographs of the instrumentation. (**A**) The electronics of the instrument. (**B**) Instrument and sensor on the buoy just before deployment. (**C**) The sensor's protective housing. (**D**) The electrodes and the vibrator [56]. Copyright 2012 Elsevier.

For the quantitative analysis of copper, the system employs square-wave anodic stripping voltammetry to ensure high-precision measurements. To monitor dissolved oxygen (DO) levels in real time, the system utilizes negative potential linear sweep voltammetry. The system maintains electrode activity and measurement accuracy by reactivating the working electrode with a specific potential sequence during measurement intervals.

The VGME measurement system's introduction into environmental monitoring, specifically for copper detection, is notable. This system efficiently detects low copper concentrations without requiring pumping equipment or chemical reagents. The introduction of a new potential sequence significantly enhances the stability and reliability of long-term measurements. With a continuous measurement cycle of up to six weeks and automatic data collection every 12 h, the device provides consistent and efficient data support for environmental monitoring.

To verify the system's stability and suitability for long-term copper monitoring, a several-week autonomous buoy deployment test was conducted in the Irish Sea, yielding preliminary data. Although the buoy's vertical movement introduced approximately 15% measurement error, normalizing the copper response to the DO response effectively reduced the long-term variability of the electrode [57]. The system successfully detected active copper concentrations ranging from 1.5 to 4 nM, with a total copper concentration of approximately 10 nM, aligning closely with laboratory voltammetry measurements [57].

3.3. An Electrochemical Analyzer for On-Site Flow Measurement

Bezerra Dos Santos et al. (2014, 2015) developed an electrochemical analyzer utilizing a potentiostat/galvanostat (PG004) as its core technology, integrated with online data transmission and global positioning systems (GPS). This integration allows for accurate geolocation of monitoring sites (Figure 4). The analyzer employs square-wave anodic stripping voltammetry (SWASV), supplemented by a flow batch analysis (FBA) system and a thermally stabilized electrochemical flow cell (EFC). Additionally, the use of a boron-doped diamond electrode (BDD) enables high-precision on-site quantitative analysis of Pb²⁺ and Cd²⁺ ions in water samples [58,59].



Figure 4. The PG004. (**A**) 1: GPS, 2: touchscreen, 3: panel with an optional keyboard, keys, and command buttons, 4: flow module, and 5: solar boards. The internal view of the PG004. (**B**) 1: 12 V batteries, 2: actuator of the flow system, 3: galvanostat board, 4: potentiostat board, 5: thermostatted control, 6: fan, 7: USB hub, 8: CPU, and 9: microcontrolled board to control the batteries. The Wi-Fi and Bluetooth board is inserted in the CPU. Flow module, with 1: EFC, 2: SVs, 3: solutions compartment, and 4: mPs [58]. Copyright 2015 Elsevier.

The team systematically explored the influence of temperature on the field analysis results of Pb²⁺ and Cd²⁺ ions and conducted a comprehensive performance evaluation of the PG004 analyzer. The experimental results show that the analyzer's detection limits for Pb²⁺ and Cd²⁺ are as low as 0.08 and 0.18 mg L⁻¹, respectively, indicating high sensitivity and the capability to analyze both ions simultaneously.

In field applications for environmental monitoring, the PG004 analyzer has been successfully deployed for on-site analysis of lake water samples, producing high-resolution voltammetric spectra with minimal noise interference. The recovery rate stabilizes within the range of 93.3% to 109%, with the waste generated from a single measurement at merely 700 mL, significantly reducing the environmental impact.

To further verify the analyzer's accuracy, a *t*-test (n = 3) was conducted by measuring the Cd²⁺ and Pb²⁺ contents in standard certified water (NIST). The results showed that at a 95% confidence level, the measured data were highly consistent with the standard values, validating the analyzer's accuracy. The instrument, equipped with a GPS receiver and solar panels for sustainable energy, facilitates fast, online, and environmentally friendly monitoring of Pb²⁺ and Cd²⁺.

3.4. Electrochemical Sensors Based on Flexible Liquid Crystal Polymers

Wang et al. developed an electrochemical sensor based on a flexible liquid crystal polymer (LCP). The core component is a bismuth (Bi) thin film electrode on an LCP substrate, designed for direct in situ measurement of zinc (II) ions. The choice of LCP as the substrate material enhances the sensor's operational stability, durability, and flexibility, making it adaptable to various installation environments. Through square-wave anodic stripping voltammetry experiments, the sensor achieved a detection limit of 1.22 nM for Zn(II) within a deposition time of 180 s [60,61].

This sensor exhibits several technical advantages, including high analytical sensitivity $(1.55 \text{ nA} \cdot \text{nM}^{-1} \cdot \text{mm}^{-2})$, a wide linear detection range (4.59 to 1071 nM), and low relative standard deviations for repeated measurements. Additionally, the sensor's efficacy in real-time in situ detection applications has been validated by monitoring Zn(II) concentrations in seawater.

To explore diverse applications, the research team integrated a flexible array comprising four LCP-based sensors into the hull of an autonomous kayak, enabling remote operation and control. This sensor array successfully captured significant fluctuations in zinc (II) concentrations in seawater, corroborated by inductively coupled plasma mass spectrometry (ICP-MS) analysis. This study supports the potential application of flexible LCP electrochemical sensors in on-site environmental monitoring.

3.5. Deep-Sea Mercury Sensor

Yamamoto et al. developed a deep-sea mercury sensor based on anodic stripping voltammetry [62]. This sensor utilizes a large gold annular disk electrode with a surface area of 402 mm², significantly enhancing its sensitivity to mercury in seawater. To improve electrodeposition efficiency, a propeller screw is installed in front of the working electrode, generating stable water flow and enhancing mercury electrodeposition efficiency.

This sensor accurately captures the peak current signal corresponding to the mercury concentration in water samples. In a 0.6 M NaCl solution, following a 20 min deposition process, the sensor achieves a minimum detection limit of 0.94 ng L^{-1} (ppt), surpassing previous detection limits. The sensor has been effectively deployed for in situ measurements of ppt-level mercury concentrations in the marine environment, corroborated by comparative analysis with cold vapor atomic fluorescence spectrometry.

However, precise calibration remains challenging under strict laboratory conditions. Future research should focus on developing novel calibration techniques to reduce reliance on large volumes of standard solutions. Additionally, in environments with high hydrogen sulfide content (e.g., near hydrothermal vents), the sensor may experience interference, necessitating performance improvements. Nonetheless, this sensor presents significant potential for monitoring mercury pollution in seawater on a broad scale.

3.6. In Situ Electrochemical Analyzer

Luther III et al. developed an in situ electrochemical analyzer (ISEA) utilizing solid microelectrode technology [63]. This analyzer enables simultaneous monitoring of various redox species and trace metals across diverse environments, including sediments, microbial mats, cultures, and hydrothermal vent-rich water columns. The ISEA can perform continuous environmental monitoring in both crewed and uncrewed modes, making it suitable for probing intricate heterogeneous environments like salt marsh sediment root zones. Data collected by the system demonstrate minimal overlap between the distribution of O_2 and

 Mn^{2+} in marine sediment pore water and microbial biofilms on metal surfaces, indicating that O_2 is not a direct oxidant of Mn^{2+} . During the analysis of hydrothermal vent water samples, the ISEA detected Fe²⁺, H₂S, and soluble FeS clusters (FeSaq), providing evidence for the roles of H₂S and FeSaq in pyrite formation. Utilizing fixed-position electrodes, a three-day continuous data collection in the Riftia pachyptila habitat revealed no significant correlation between O_2 and H₂S but a general correlation between H₂S and temperature.

In summary (Table 1), the current in situ heavy metal detection instruments based on electrochemical stripping voltammetry have a solid research foundation and have been deployed in various waters, from offshore to deep-sea environments. These instruments are calibrated using the standard addition method either in the laboratory or on-site, and the chemical cleaning method is employed for instrument maintenance. The reuse of the instrument mainly depends on the renewal of the electrodes; after electrode renewal, these instruments can be reused. However, these instruments still exhibit certain limitations. VIP systems lead in terms of technological maturity, with commercial products already available, yet their technology requires further improvement and optimization to cater to broader applications. For instance, while the VIP and its upgraded version TracMetal can detect elements such as Cu(II), Pb(II), Cd(II), Zn(II), and As(III), their operational depth is limited to 100 m, restricting deeper water applications. The advantage of the VGME lies in its short enrichment time of only 5 min, suitable for detecting Cu(II) with low concentration requirements. However, its operational depth is limited to 40 m, thus restricting its application range. The PG004 can rapidly detect Pb(II) and Cd(II) in surface waters, but its detection limits of 0.39 and 1.6 mM do not meet the requirements for trace metal detection. Both the LCP and the deep-sea mercury sensor currently detect only one element, limiting their functionality. The ISEA can operate at depths of 6000 m in deep-sea environments; however, its detection limits for Mn(II) and Fe(II) are as high as 5 and 10 μ M, suitable primarily for hydrothermal/cold spring areas and challenging for detecting trace metals in conventional seawater environments.

Instrument	Analyte of Interest	Pre-Concentration Time/min	Limit of Detection	Working Depth	Ref.
VIP	Cu(II)/Pb(II)/Cd(II)/Zn(II)	15	0.5 nM/0.25 nM/0.03 nM/0.04 nM	100 m	[49]
TracMetal	As(III)	10	1.5 nM	100 m	[50]
VGME	Cu(II)	5	4 nM	40 m	[55]
PG004	Pb(II)/Cd(II)	5	0.39 mM/1.6 mM	Surface	[57]
LCP	Zn(II)	3	1.22 nM	Surface	[60]
Deep-sea mercury sensor	Hg(II)	20	4.69 nM	1000 m	[62]
ISEA	Mn(II)/Fe(II)	10	5 μM/10 μM	6000 m	[63]

Table 1. Summary of in situ voltammetry analyzers.

4. Development of Electrodes

4.1. Microelectrode Arrays

Microelectrode array technology has become a central focus in electroanalytical chemistry, particularly for detecting trace metals. This technology enhances mass transfer on the electrode surface by leveraging the hemispherical diffusion characteristics of microelectrodes, mimicking a convective environment. This allows for the rapid acquisition of stable non-zero current readings, reducing the need for stirring and making it highly suitable for in situ sensing applications. Additionally, the low iR drop and high signal-to-noise ratio inherent to microelectrode arrays ensure accurate measurements in high-resistance environments, such as low ionic strength media, without the need for additional supporting electrolytes or complex sample pretreatment steps [46–48].

The Tercier-Waeber team has been instrumental in advancing microelectrode array (MEA) technology for the detection of heavy metals in natural waters [64]. Over the years, their innovative approaches and applications have significantly contributed to the field of environmental monitoring. Noël et al. (2003) laid the groundwork by integrating

complexing gels with MEAs to directly detect free metal ion concentrations in natural waters. This early work highlighted the potential of MEAs in providing accurate and real-time data on metal ion dynamics, establishing a foundation for future innovations [65]. In 2009, Tercier-Waeber, Hezard, and Masson advanced the application of MEAs by monitoring the diurnal evolution of dynamic metal species in the Riou-Mort River and bioavailable inorganic mercury in marine systems. This study demonstrated the capability of MEAs to capture temporal variations in metal concentrations, essential for understanding environmental processes and impacts [47]. Tercier-Waeber et al. (2021) made notable progress in environmental monitoring through their development of a gel-integrated nanostructured gold-based interconnected microelectrode array (MEA) designed for continuous in situ arsenite monitoring in aquatic environments (Figure 5) [50]. This advanced sensor allowed for high-resolution and real-time tracking of arsenite levels, significantly improving the accuracy of measurements in dynamic aquatic systems. Additionally, they applied similar gel-integrated nanostructured gold-based MEAs for the detection of bioavailable inorganic mercury in marine environments. The sensors demonstrated high sensitivity and specificity, crucial for evaluating mercury bioavailability and understanding its ecological risks. These innovations represent a significant leap forward in the monitoring and assessment of hazardous substances in water systems [50,54]. Most recently, Creffield et al. (2023) focused on addressing the challenge of sensor fouling. They designed an on-chip antifouling gel-integrated MEA for high-resolution quantification of the nickel fraction available for bio-uptake in natural waters. This advancement ensures the reliability and accuracy of MEAs in complex and biofouling-prone environments [51].

A Process Flow steps	Cross section
0. Silicon wafer passivated with 200 nm Si ₃ ? Pressure Chemical Vapor Deposition (LP	I₄ by Low CVD) (200 nm)
1. Ta / Ir sputtering (20 nm / 150 to 200 nm)	
2. Ir / Ta Ion Beam Etching (IBE; dry etchin	g)
 Si₃N₄ Plasma-Enhanced Chemical Vapor (PECVD) (200 nm) 	Deposition
4. Si_3N_4 Deep Reactive Ion Etching (DRIE;	lry etching)
5. EPON SU-8 Photolitography (150 μm / 30	10 μm)



Figure 5. (**A**) Thin film process flow steps for the manufacturing of the on-chip interconnected Ir-based microdisk arrays; (**B**) scheme of a chip incorporating an interconnected Ir microdisk array and an Ir microcounter electrode [50]. Copyright 2021 Elsevier.

Microelectrode arrays (MEAs) are pivotal in heavy metal detection due to their high sensitivity and spatial resolution (Table 2), enabling trace-level detection and localized monitoring in complex environmental matrices. They facilitate real-time, continuous monitoring,

crucial for understanding temporal variations and responding promptly to environmental changes. MEA miniaturization allows integration into compact, portable devices, enhancing accessibility and applicability in diverse environmental settings. Advances in electrode materials enable selective detection amidst complex matrices, reducing interference and improving accuracy [64,65]. Challenges include fouling from environmental species, complex and costly fabrication, and the need for improved durability in harsh conditions. Future improvements must focus on robust antifouling strategies, novel materials, nanotechnology applications, integration with data analytics for real-time processing, standardized protocols for reliability, and expanding environmental applications beyond laboratories. Addressing these challenges will enhance the effectiveness of MEAs in environmental monitoring, emphasizing continued research and innovation in sensor technology and data integration.

Electrode	Analyte of Interest	Technique	Pre-Concentration Time/min	Limit of Detection	Ref.
GIME	Cu(II), Pb(II), Cd(II), Zn(II)	SWASV	15	0.04 nM/0.03 nM/0.25 nM/0.5 nM	[49]
AuNS-CSPE	As(III)	SWASV	3	40 nM	[50]
Au MEA	Cu(II)	DPASV	5	0.013 nM	[56]

4.2. Screen-Printed Electrodes

Screen-printed electrodes (SPEs) have garnered significant attention in electrochemical stripping analysis, particularly for detecting trace heavy metals. This technology is pivotal in environmental monitoring, providing detailed insights into heavy metal ion distribution and enabling in situ analysis [66–72].

García-González et al. (2014) developed dual screen-printed electrodes featuring elliptic working electrodes arranged either parallel or perpendicular to the strip, demonstrating improved electrochemical performance for various analytes. This innovative design highlights the potential of SPEs in achieving precise and reliable measurements in complex matrices [73]. In a pioneering study, de Souza et al. (2015) introduced back-to-back screenprinted electroanalytical sensors specifically designed for heavy metal ion sensing. These sensors exhibited remarkable performance in the detection of trace metal ions, underscoring the robustness and versatility of SPEs in environmental and industrial applications [74]. Further exploring the potential of SPEs, Jadav et al. (2018) developed a silver/carbon screen-printed electrode for the rapid determination of vitamin C in fruit juices. Although not directly related to heavy metal detection, this study demonstrated the adaptability and broad applicability of SPEs in diverse analytical contexts, which can be translated to heavy metal analysis [75]. Ong et al. (2021) provided a critical review highlighting the electro-reactivity of screen-printed nanocomposite electrodes. Their study emphasized the role of SPEs in safeguarding the environment from trace metals, underscoring the electrode's capability to detect and quantify metals at low concentrations (Figure 6) [76]. Recent innovations have further enhanced SPE performance. Birara et al. (2023) explored the use of bismuth/poly(bromocresol purple)-modified screen-printed carbon electrodes for quantifying Cd(II) and Pb(II) in wastewater. Their findings underscored the electrode's applicability in complex matrices, demonstrating robust analytical performance [77]. Furthermore, Pasakon et al. (2023) investigated screen-printed ionic liquid/graphene electrodes for simultaneous electrochemical sensing of Cd²⁺ and Pb²⁺. This study highlighted the electrodes' versatility in different environmental conditions, offering insights into optimizing sensor design for enhanced detection capabilities [78]. Zhang et al. (2024) developed a screen-printed electrode incorporating a bismuth/graphene oxide hybrid, enabling simultaneous detection of cadmium and lead ions. This modification enhances the sensitivity and selectivity, which are crucial for accurate environmental monitoring [79].



Figure 6. Common geometries in SPE: (**a**) micro-disc [75], (**b**) micro-band [80], (**c**) micro-array [81], (**d**) dual SPE in perpendicular [73] (**d-i**) and parallel (**d-ii**) and (**e**) double-sided SPE [74]. Copyright 2021 Elsevier.

However, SPEs face challenges such as batch-to-batch reproducibility (Table 3), limited stability with prolonged use, and sensitivity to environmental conditions, necessitating ongoing refinement efforts. Future research, as suggested by Pasakon et al. (2023), aims to improve SPEs through innovations like ionic liquids and graphene integration to enhance stability and sensitivity in detection. Advancements in nanomaterials and surface modifications offer promising avenues for enhancing SPE performance, including increased sensitivity, selectivity, and operational lifespan [82].

Table 3. Typical screen-printed electrodes.

Electrode	Analyte of Interest	Technique	Pre-Concentration Time/min	Limit of Detection	Ref.
Bi-P-SPCE	Pb(II)/Cd(II)	SWASV	3	6.32 nM/13.8 nM	[79]
4-CP/SPCE	Pb(II)/Cd(II)	DPASV	5	0.65 nM/0.882 nM	[83]
GN-SPCE	Hg(II)	SWASV	5	1.65 nM	[84]

4.3. Carbon Electrodes

Modified carbon electrodes, particularly glassy carbon electrodes, and carbon paste electrodes, are pivotal in metal stripping voltammetry for the precise determination of low-concentration metal ions (Figure 2). The choice of electrode material is crucial for measurement accuracy. Carbon electrodes have emerged as versatile tools in electrochemical sensing due to their excellent conductivity, surface area, and compatibility with various modifications aimed at enhancing sensitivity and selectivity [85–88].

Zhang et al. (2016) investigated size-dependent electrochemical detection of trace heavy metal ions using nano-patterned carbon sphere electrodes. Their study demonstrated that the size and surface properties of carbon spheres significantly influence the sensitivity and detection limits of heavy metals, emphasizing the importance of electrode nanostructuring in enhancing analytical performance (Figure 7) [89]. Xhanari et al. (2018) presented the validation and optimization of an in situ copper-modified glassy carbon electrode. This work highlighted the enhanced electrochemical performance for heavy metal detection achieved through modification with copper, which facilitated better electron transfer kinetics and improved detection limits [90]. Tüzün and Atun (2023) investigated the use of carbon paste electrodes modified with titania nanoparticles for individual and simultaneous determination of heavy metal ions. Their study emphasized the role of nanostructured materials in improving electrode performance, offering insights into the optimization of detection methods for environmental monitoring [91]. Finšgar and Rajh (2023) employed a factorial design and simplex optimization approach to develop a bismuth film glassy carbon electrode for Cd^{2+} and Pb²⁺ determination. Their work underscored the importance of electrode surface modification and optimization strategies in achieving reliable and accurate heavy metal sensing [92]. Roushani et al. (2024) explored an aminoclay-based porous covalent organic polymer/multi-walled carbon nanotube-modified glassy carbon electrode for the detection of Pb²⁺, Cu²⁺, and Hg²⁺. Their research highlighted the use of novel polymer–nanotube composites to enhance the electrode's sensitivity and stability, which are crucial for multi-metal ion detection [93].



Figure 7. (a) SEM image of the self-assembled carbon sphere electrodes. (b) The scheme of the first layer (left) and ordered structures (right) of the hexagonal close-packed structures model. (c) The process of the electrochemical detection of trace Pb(II) in an aqueous solution using SWASV [89]. Copyright 2016 Elsevier.

Carbon electrodes are widely used in heavy metal detection due to their excellent conductivity and chemical stability, ensuring reliable electrochemical responses (Table 4). Their high surface area allows effective modification with nanomaterials and polymers, enhancing selectivity and sensitivity for specific analytical needs. Additionally, carbon materials are cost-effective and easy to prepare, facilitating scalable deployment in environmental monitoring and industrial applications. However, challenges such as sensitivity limitations for trace heavy metal ions require advanced modification strategies to improve detection limits. Issues like electrode lifespan and stability under varying chemical conditions also impact long-term reliability. Complex sample matrices in environmental samples pose challenges to accurate real-time monitoring using carbon-based sensors. Future research should focus on enhancing sensitivity through optimized surface modifications with graphene, metal nanoparticles, or conducting polymers to improve signal-to-noise ratios and lower detection limits. Improving electrode stability and lifespan can be achieved by exploring new carbon composites or protective coatings resistant to harsh conditions. Integrating advanced signal processing techniques and selective recognition elements can mitigate matrix effects and enhance specificity in heavy metal detection. These advancements are crucial for expanding the application of carbon electrodes in environmental monitoring and industrial quality control, reinforcing their pivotal role in electrochemical sensing [94–98].

Electrode	Analyte of Interest	Technique	Pre-Concentration Time/min	Limit of Detection	Ref.
GCE/KHEP	Pb(II)/Cu(II)	SWASV	3	1.07 μM/1.94 μM	[88]
TMCP	Pb(II)/Cu(II)/Hg(II)	ASV	5	1.65 nM/0.56 Nm/15.26 nM	[91]
CuFE	Pb(II)	SWASV	1.5	9.65 nM	[92]

Table 4. Typical carbon electrodes.

4.4. Bismuth Electrodes

Bismuth electrodes are increasingly utilized in electrochemical sensing due to their unique attributes, such as low toxicity, high hydrogen evolution overpotential, and wide potential window [99].

Promsuwan et al. (2024) developed a novel single-drop electrodeposition method to fabricate nanoneedle-like bismuth on disposable graphene electrodes. Their work demonstrated efficient on-site electrochemical detection of cadmium and lead, leveraging the enhanced electrocatalytic properties of bismuth nanoneedles for sensitive and selective detection [100]. Muluneh et al. (2023) investigated the use of a bismuth-modified glassy carbon electrode for the determination of lead (II) and cadmium (II) in water-based paints. This highlighted the applicability of anodic stripping voltammetry for accurate quantification of heavy metal ions, showcasing the electrode's effectiveness in complex sample matrices (Figure 8) [101]. In a different application, Liu et al. (2024) developed integrated equipment utilizing smartphone control and machine-learning algorithms for the automated detection of bioavailable heavy metals in soils. Although not directly focused on bismuth electrodes, their innovative approach underscores the evolving technologies in environmental monitoring and heavy metal detection [102]. Martynov et al. (2024) explored the determination of indium using adsorptive stripping voltammetry at a bismuth film electrode with a combined electrode system facilitating medium exchange. Published in Talanta, their study highlighted advancements in electrode design and methodology to achieve sensitive and reliable analysis of heavy metals [103].



Figure 8. Simultaneous determination of lead (II) and cadmium (II) in water paint using a bismuthmodified gassy carbon electrode with anodic stripping voltammetry [101]. Copyright 2014 Elsevier. Copyright 2023 Elsevier.

The bismuth electrode represents an ideal alternative to traditional mercury electrodes due to its outstanding electrocatalytic performance, particularly in the realm of heavy metal detection (Table 5). It enables the sensitive and selective detection of ions like cadmium and lead, facilitated by nanostructured forms such as nanoneedles that enhance surface area and electron transfer efficiency. Moreover, bismuth electrodes demonstrate robust chemical stability across varying conditions, ensuring reliable performance in prolonged analytical use. However, challenges include susceptibility to fouling and surface passivation in complex sample matrices, compromising long-term stability and sensor effectiveness. Achieving consistent reproducibility in electrode fabrication remains critical for reliable analytical results. While sensitivity to trace levels of heavy metals has improved, further enhancements are needed for ultra-trace detection applications. Future research should

focus on innovative approaches to overcome these challenges. These include refining the bismuth electrode design through advanced nanostructuring techniques like controlled deposition of bismuth nanomaterials to enhance surface morphology and electrochemical activity. The integration of novel materials or hybrid structures can mitigate fouling effects and enhance stability in challenging environmental conditions. Optimizing surface modification strategies with functional nanomaterials or conducting polymers holds promise for enhancing sensitivity and selectivity, enabling real-time and precise monitoring of heavy metals in diverse environmental samples [104–109].

Electrode	Analyte of Interest	Technique	Pre-Concentration Time/min	Limit of Detection	Ref.
P-GE	Pb(II)/Cd(II)	SWASV	3	10.14 nM/31.2 nM	[100]
BGCE	Pb(II)/Cd(II)	SWASV	2	60 nM/130 nM	[101]
Bismuth film electrode	Pb(II)	SWASV	3	0.04 nM	[104]

Table 5. Typical bismuth electrodes.

4.5. Lab-on-a-Chip (LOC)

Lab-on-a-chip (LOC) technology has emerged as a revolutionary approach in chemical and biological analysis, providing miniaturized, automated, and highly efficient platforms for diverse applications. This review synthesizes recent advancements and seminal contributions in LOC technology, drawing insights from key references [110–117].

Jung et al. (2011) developed a polymer-based LOC sensor with microfabricated planar silver electrodes for continuous and on-site heavy metal measurement. Their research focused on achieving real-time monitoring capabilities, emphasizing the scalability and cost-effectiveness of polymer-based microfluidic platforms [118]. Zhao et al. (2014) introduced a portable LOC system for gold-nanoparticle-based colorimetric detection of metal ions in water. Their work demonstrated the integration of nanoparticle-based assays for rapid and sensitive detection, suitable for field deployment and environmental monitoring [119]. Chałupniak and Merkoçi (2017) presented a graphene oxide-poly(dimethylsiloxane)-based LOC platform for heavy metal preconcentration and electrochemical detection. Their study highlighted the advantages of graphene oxide in enhancing preconcentration efficiency and sensitivity in complex environmental samples (Figure 9) [120]. Wang et al. (2021) developed an electrochemical paper-based microfluidic device for online isolation of proteins and direct detection of lead in urine. Their work demonstrated the feasibility of integrating sample preparation and detection in a portable format, emphasizing the potential for point-of-care applications [121].

Lab-on-a-chip (LOC) electrodes revolutionize heavy metal detection with their compact integration of multiple analytical functions, reducing sample volume and analysis time (Table 6). This miniaturization enhances efficiency and portability, catering to on-site and point-of-care applications. Optimized microfluidic channels and electrode configurations enable LOC electrodes to achieve high sensitivity and selectivity, crucial for accurately detecting trace levels of heavy metals. However, despite these strengths, LOC technology faces significant challenges that limit its widespread adoption. Complex fabrication processes and high initial costs remain major barriers, impeding accessibility for many potential users and applications. Moreover, integrating complex sample matrices into microfluidic systems without interference poses a substantial hurdle, affecting the reliability and accuracy required for real-world applications. Addressing these challenges requires continuous improvement of microfabrication techniques to streamline production and reduce costs. Exploring novel materials and enhancing microfluidic control systems are essential steps towards enhancing the reliability, scalability, and versatility of LOC devices. These advancements are crucial for expanding the capabilities of LOC electrodes in environmental monitoring, healthcare diagnostics, and industrial quality control, ensuring they can effectively meet the demands of diverse analytical challenges in the field of heavy metal detection [122–124].



Figure 9. (a) Microfluidic channels of the graphene oxide–polydimethylsiloxane (GO-PDMS) chip. A—inlet section of the chip, B—middle section, C—outlet section. (b) GO-PDMS chip device. Despite the high content of GO, the composite maintains typical physical properties of PDMS like mechanical durability and elasticity [120]. Copyright 2017 Elsevier.

Table 6. Typical lab-on-a-chip devices.

Electrode	Analyte of Interest	Technique	Pre-Concentration Time/min	Limit of Detection	Ref.
μPAD	Pb (II)	SWASV	2	43.4 nM	[119]
GO-PDMS	Pb(II)	SWASV	5	2.14 nM	[120]
LODs	Pb(II)/Al(III)	SWASV	3	144.8 nM/3.3 nM	[121]

In summary (Table 7), MEAs offer high sensitivity and low detection limits, making them suitable for in situ measurements, but they are complex to fabricate, expensive, and are typically reusable. SPEs are low-cost, easy to produce, portable, and disposable, though they generally have lower sensitivity and shorter lifespans. Carbon Electrodes are stable, have a wide potential window, and can be enhanced with nanomaterials, but they may require surface modification, have higher detection limits, and are reusable. Bismuth electrodes are an environmentally friendly, non-toxic alternative to mercury electrodes, offering good sensitivity and low detection limits, but they can be less stable, and are also reusable. Lab-on-a-Chip (LOC) devices integrate multiple functions and require small sample volumes, making them portable and suitable for on-site analysis, but they involve complex and costly fabrication processes and can be either single-use or reusable depending on the design.

Table 7. Comparison table of different types of electrodes.

Electrode Type	Advantages	Disadvantages	Re-Use
Microelectrode Arrays (MEA)	High sensitivity, low detection limits, suitable for in-situ measurements.	Complex fabrication, higher cost, potential for electrode fouling.	Yes, several days to two weeks, long-term functionality can be maintained by regenerating the modification.
Screen-Printed Electrodes (SPE)	Low cost, easy to mass-produce, portable, disposable.	Lower sensitivity, higher detection limits, shorter lifespan.	No, few hours, single-use.
Carbon Electrodes (CE)	Stable, wide potential window, good conductivity, modifiable with nanomaterials.	May require modification, higher detection limits, potential for fouling.	Yes, several weeks to months, long-term functionality can be maintained by regenerating the modification.

Electrode Type	Advantages	Disadvantages	Re-Use
Bismuth Electrodes	Environmentally friendly, non-toxic, good sensitivity, low detection limits.	Less stable in some conditions.	Yes, several weeks to months, long-term functionality can be maintained by regenerating the modification.
Lab-on-a-Chip (LOC)	Integration of multiple functions, small sample volume, portable, on-site analysis.	Complex fabrication, higher costs, limited robustness and reproducibility.	Varies, few hours to several weeks.

Table 7. Cont.

5. Trends and Future Directions

5.1. Advancements in Electrode Research

Extensive research is dedicated to advancing electrode materials to enhance analyzer performance. Carbon nanomaterials, including carbon nanotubes and graphene, are at the forefront of current research due to their expansive specific surface area and superior conductivity [125]. Composite materials that combine metal oxides with conductive polymers also exhibit significant electrochemical activity and stability [126,127]. Recent years have seen the emergence of biosensor materials exhibiting heightened selectivity and sensitivity through various biomolecule applications. Moreover, emerging nanomaterials like metal–organic frameworks (MOFs) and quantum dots garner attention for their distinctive advantages as electrode materials [128–133]. This underscores the need for continued in-depth research into high-performance electrode materials to advance the innovation and application of underwater in situ heavy metal monitoring technology.

5.2. Intelligent Monitoring and Data Analytics

Technological advancements are enabling intelligent monitoring and data analytics in underwater in situ heavy metal voltammetry analyzers. The advent of Internet of Things (IoT) technology facilitates real-time, precise monitoring of underwater heavy metal concentrations alongside remote data transmission. This advancement streamlines operational processes, ensuring heightened measurement accuracy and operational efficiency. Furthermore, coupling data mining with artificial intelligence (AI) analysis techniques enables profound data exploration, unveiling pollution sources and trends while enhancing analysis accuracy and efficiency. Integration with geographic information systems (GIS) enables comprehensive three-dimensional visualization of underwater environmental pollution. These transformative technologies propel ongoing research, promising more efficient and precise support for environmental protection and scientific inquiry [26,134].

5.3. Interdisciplinary Collaboration and Technological Innovation

The fusion of environmental science and engineering technology is crucial for advancing underwater in situ heavy metal voltammetry analyzers. Environmental science elucidates the mechanisms underlying heavy metal pollution, furnishing crucial insights for instrument development and material selection. Engineering technologies, encompassing sensing, micro/nanotechnology, and the IoT, fuel the optimization of analyzer performance. Notably, IoT technology enables remote real-time monitoring, amplifying monitoring efficiency. Interdisciplinary collaboration fosters technological innovation, exemplified by biosensors inspired by biological systems. This collaborative framework drives technological progress, facilitating more efficient and precise monitoring of heavy metal pollution, thereby amplifying contributions to environmental conservation and human health [43,135–137].

6. Conclusions

This review systematically examines recent advancements in underwater in situ trace metal analysis technology. Specifically, it is the first to comprehensively cover nearly all types of underwater in-situ trace metals voltammetry analyzers currently available, providing significant reference value for research in the related field.

Despite significant advancements, current in situ trace metals detection instruments utilizing electrochemical stripping voltammetry have established a robust research foundation and are deployed in diverse aquatic environments, ranging from offshore to deep-sea settings. However, these instruments still possess inherent limitations. Presently, no instruments, including the commercial VIP system, are capable of operating effectively at depths exceeding 1000 m while achieving accuracy at the parts-per-trillion (ppt) level. Furthermore, besides the VIP system's ability to detect multiple metal elements, other instruments are constrained to identifying no more than three trace metals.

In current electrode technology, microelectrode arrays (MEAs) enable trace detection and localized monitoring in complex environmental matrices. However, they face challenges such as environmental species contamination, complex and expensive fabrication processes, and durability under harsh conditions. Carbon electrodes are widely used for trace metals detection due to their excellent conductivity and chemical stability. Future research should focus on optimizing surface modifications using graphene, metal nanoparticles, or conductive polymers to enhance the signal-to-noise ratio and lower the detection limit. Bismuth electrodes, as ideal substitutes for mercury electrodes, benefit from nanostructures such as nanoneedles that enhance surface area and electron transport efficiency. However, challenges include contamination and surface passivation in complex samples. Future research should explore advanced nanostructuring techniques and the integration of novel materials to overcome these challenges and improve the sensitivity and selectivity of bismuth electrodes in trace metals detection. Lab-on-a-chip (LOC) electrodes have revolutionized trace metals detection through their compact multifunctional integration. Nonetheless, complex fabrication processes and high costs limit their widespread application. Future research should aim to improve microfabrication technologies, explore new materials, and enhance microfluidic control systems to expand the applicability of LOC electrodes in environmental monitoring, medical diagnostics, and industrial quality control.

In summary, despite the significant potential of electrochemical sensors for in situ detection of trace metals in seawater, there is still a lack of sufficient in situ experimental data to validate their practical application. Although there have been relevant research and development advancements in this field, most achievements remain at the laboratory stage and have not been widely applied in real-world environments. Currently, only the VIP system has successfully achieved commercialization, but its market penetration and application scope are still limited. Electrochemical sensors hold remarkable potential for driving innovations in seawater analysis technology. However, to realize this goal, it is essential to clearly define the research and development pathways and conduct specialized in-depth studies.

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