COMPARATIVE ANALYSIS BETWEEN TRADITIONAL AND ELECTROCHEMICAL METHODS FOR THE MULTIELEMENT DETERMINATION OF HEAVY METALS: ADVANCES AND PERSPECTIVES

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ABSTRACT

This article presents a comparative analysis between traditional and electrochemical methods for the multielemental determination of heavy metals in environmental and biological samples. Recent advances in the application of electrochemical techniques—such as voltammetry—are discussed, highlighting improvements in analytical sensitivity, selectivity, and speed. The advantages and limitations of each approach are examined, and future perspectives are provided for the development of more efficient and sustainable electrochemical methods for heavy metal detection.

Keywords: Electrochemistry · Sensors · Multielemental analysis · Environment.

INTRODUCTION

The determination of heavy metals in environmental and biological samples is essential for assessing environmental quality and preventing risks to human health [1–4]. Heavy metal determination represents a crucial aspect in evaluating environmental quality and safeguarding human health. These elements—including heavy metals such as lead, mercury, cadmium, and arsenic—are highly relevant environmental and public health contaminants due to their persistence, bioaccumulative potential, and severe toxic effects on both ecosystems and human health.

Delving into this topic requires exploring the multiple aspects related to the presence, distribution, effects, and mitigation strategies of heavy metals in the environment and living organisms.

First, the presence of heavy metals in the environment arises from diverse sources, including industrial, agricultural, mining, and domestic activities [5–8]. These metals can enter the environment through industrial discharges, mining waste, pesticides, fertilizers, and other chemical products, as well as through natural processes such as soil erosion and volcanic activity. Once released into the environment, heavy metals can persist for extended periods and accumulate in soils, sediments, water, and biological tissues, thereby increasing the risk of human exposure and ecological damage [9–13].

Regarding human health effects, exposure to heavy metals can lead to a wide range of adverse outcomes, ranging from acute intoxication to chronic conditions such as cancer, neurological disorders, kidney damage, cardiovascular diseases, and congenital anomalies [13–16]. These effects can be particularly severe in vulnerable populations, including children, pregnant women, the elderly, and socioeconomically disadvantaged communities who may experience higher exposure through contaminated food, drinking water, or occupational contact.

Beyond their direct impact on human health, heavy metal contamination can also have significant consequences for terrestrial and aquatic ecosystems. The accumulation of heavy metals in soils and sediments affects soil quality, nutrient availability, and biodiversity, potentially causing cascading effects on ecosystems and the ecosystem services they provide, such as food production, water purification, and climate regulation [17–20].

To address these challenges, comprehensive strategies for monitoring, risk assessment, and management of heavy metal contamination are required. This includes implementing environmental monitoring programs to identify contamination sources, assess contamination magnitude, and guide decision-making in environmental management.

Therefore, determining heavy metals in environmental samples constitutes a fundamental pillar to understand and address the risks inherent to contamination by these elements. Exploring the aspects of heavy metal analysis, particularly in multielemental approaches, involves delving into the complexity of analytical processes and the diversity of factors influencing result accuracy and reliability.

From this perspective, the primary objective of this article arises from the pressing need to conduct an exhaustive comparative assessment between traditional and electrochemical methods for heavy metal determination. Such comparison aims not only to identify the inherent strengths and weaknesses of each analytical approach but also to highlight opportunities to optimize the efficiency and reliability of electrochemical methods in multielemental heavy metal detection.

Traditional Techniques

For decades, traditional methods have been the cornerstone in the determination of heavy metals, employing established techniques such as atomic absorption spectroscopy (AAS) [21–25], inductively coupled plasma mass spectrometry (ICP-MS) [26–30], and atomic emission spectroscopy (AES) [31–33]. These techniques are valued for their high sensitivity and specificity, enabling precise quantification of multiple elements in a single sample, and have become indispensable in environmental, toxicological, and industrial control applications. Their ability to detect trace levels of heavy metals has been essential for monitoring contamination and assessing risks to public health and ecosystems.

Despite their clear advantages, traditional methods present limitations that constrain their applicability in certain contexts. One major barrier is the high cost associated with acquiring and maintaining instrumentation. Equipment such as ICP-MS requires significant investment not only for initial purchase but also for routine operation and maintenance. This limits accessibility for smaller laboratories or those with restricted budgets, potentially affecting the scope of studies that depend on these tools.

In addition to financial constraints, operational complexity is another limiting factor. Operating ICP-MS or AES equipment requires highly qualified personnel experienced in advanced analytical techniques, increasing reliance on specialized staff and posing challenges in settings where expertise is scarce. This need for specialized personnel further raises operational costs and can slow analysis implementation in urgent situations.

Sample preparation is another significant challenge. In many cases, this process is laborious and time-consuming, involving sample digestion and the use of a wide range of chemical reagents. Beyond increasing costs and prolonging turnaround times, sample preparation also generates hazardous waste and consumes large amounts of chemicals, raising environmental and safety concerns. This is especially problematic in a world increasingly focused on sustainability and tighter environmental regulations.

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Technically, while traditional techniques are highly effective for detecting individual metals, they may struggle with analyzing complex samples containing mixtures of elements at varying concentrations. This can limit their applicability in scenarios requiring precise and rapid multielemental assessment. Furthermore, the time required to complete a full analysis can be considerable, reducing efficiency in situations demanding rapid response, such as environmental contamination events or public health emergencies.

Therefore, although traditional techniques have been fundamental in heavy metal determination and remain powerful tools in many contexts, their limitations in terms of costs, infrastructure, time, and environmental considerations are obstacles that cannot be ignored. Consequently, it is crucial to explore technological alternatives that can overcome these disadvantages. Innovations in detection technologies, such as the use of portable sensors, nanomaterial-based techniques, and more sustainable approaches, can offer promising solutions. The miniaturization of analytical devices, automation of processes, and development of methodologies that reduce the use of toxic reagents are key directions in which current research is focused. These alternatives aim not only to maintain or improve the precision and sensitivity of traditional techniques but also to make them more accessible, efficient, and environmentally friendly. The evolution toward more sustainable and accessible techniques is not merely a technological need but also a priority in addressing global contamination and environmental protection challenges.

Electrochemical Techniques

In contrast to traditional methods, electrochemical techniques have emerged as promising and versatile alternatives for heavy metal determination. Voltammetry, a widely used electroanalytical technique, offers numerous substantial benefits driving its growing adoption in scientific research and environmental monitoring.

One of the main appeals of electrochemical methods lies in their inherent simplicity and relatively low cost in terms of instrumentation and reagents. Unlike the sophisticated and expensive equipment required for many traditional techniques, voltammetric instruments are typically simpler and more affordable, making them accessible to a wide range of research laboratories, even those operating under budget constraints. This accessibility democratizes analytical technology and fosters collaboration across diverse scientific and academic communities.

Beyond affordability, sample preparation for electrochemical analysis tends to be simpler and faster compared to traditional methods. The streamlined preparation procedures not only save time and resources but also reduce the likelihood of human error and increase the overall efficiency of the analytical process. This is particularly valuable in settings requiring high throughput and rapid response, such as real-time water quality monitoring or environmental emergency situations.

Another distinctive advantage is their ability to perform in situ measurements, enabling continuous and real-time monitoring of heavy metal contamination in the environment [34–37]. This real-time monitoring capacity is essential for understanding temporal fluctuations in heavy metal concentrations and identifying acute contamination events requiring immediate action. Additionally, the ability to conduct in situ measurements reduces the need for sample transport to laboratories, further lowering costs and turnaround times.

In addition to ease of use and real-time monitoring, electrochemical methods exhibit exceptional sensitivity and selectivity in detecting trace levels of heavy metals in complex samples. Their capability to detect extremely low concentrations with high precision and selectivity makes them invaluable tools in environmental and biomedical research. This sensitivity and selectivity enable early contaminant detection and precise risk assessment for public health and the environment, facilitating effective control and mitigation measures. Likewise, the potential for simultaneous multielemental measurements and high instrumental versatility makes electrochemical techniques well-suited for developing integrated analytical platforms capable of comprehensive characterization of contaminants in complex environmental and biological matrices.

Several studies have supported the efficacy of multielemental electrochemical techniques. The paper by J. Wang and collaborators [38] describes the development of an electrochemical sensor based on a bismuth-modified mercury amalgam electrode used in anodic stripping voltammetry to detect heavy metals such as lead and cadmium at very low concentrations. One of the main advantages of this sensor is its high sensitivity, enabling trace-level metal detection and improving analytical accuracy compared to traditional mercury electrodes. Furthermore, the replacement of mercury with bismuth greatly reduces toxicity issues, making it safer for both operators and the environment.

Another notable advantage is the electrochemical stability of the sensor, which provides more consistent and repeatable responses, ensuring the reliability of results under various experimental conditions. In addition, this sensor has demonstrated its ability to perform effectively in complex matrices such as environmental water samples, highlighting its usefulness in practical environmental monitoring applications for multielemental heavy metals such as lead and cadmium.

Li [39] reports on the development of an electrochemical sensor based on porous cerium–zirconium (Ce–Zr) oxide nanospheres for the sensitive and interference-free detection of lead ions (Pb^{2+}) in wastewater. The use of these nanomaterials enhances adsorption capacity and the active surface area of the sensor, leading to improved sensitivity. The catalytic properties of cerium, combined with the stability and robustness of zirconium, make the sensor effective in complex aqueous environments containing other metal ions that may interfere. This sensor supports precise determination of Pb^{2+} without interference from other substances, offering high sensitivity, specificity, and stability—making it valuable for environmental monitoring during wastewater treatment and environmental protection against heavy metal pollution.

Researcher Juan C. M. Gamboa [40] focuses on the development and application of a printed electrode modified with carbon nanotubes and gold nanoparticles for the simultaneous determination of zinc, lead, and copper. This methodology represents a significant advance in analytical electrochemistry, enabling efficient and precise multielemental analysis in environmental and biological samples.

A key advantage of this method is its ability to detect and quantify multiple heavy metals in a single analytical run. Traditionally, heavy metal determination required multiple individual assays, consuming considerable time and resources. However, Gamboa's modified electrode enables simultaneous determination of zinc, lead, and copper, saving time and increasing analytical efficiency.

Beyond its multielement capability, this method also offers additional notable benefits. The incorporation of carbon nanotubes and gold nanoparticles enhances the electrode's sensitivity and selectivity, resulting in lower limits of detection and higher measurement precision. This feature is critical when accurate detection of trace-level heavy metals is required, such as in environmental monitoring or drinking water quality assessment.

nother important benefit is the versatility and usability of the printed electrode. This type of electrode can be economically mass-produced and used in a variety of environments, ranging from research laboratories to field applications. Furthermore, the ability to perform measurements directly in complex samples, without requiring elaborate sample preparations, simplifies the analytical process and facilitates its application in environmental monitoring and public health studies.

Another noteworthy article is "Simultaneous determination of ultra-trace lead and cadmium at a hydroxyapatite-modified carbon ionic liquid electrode by square-wave stripping voltammetry" by Li (2009) [41]. This work presents an innovative and promising approach for the concurrent determination of lead and cadmium at ultra-trace levels. The study stands out for its detailed focus on applying square-wave anodic stripping voltammetry in combination with a carbon electrode modified with hydroxyapatite and ionic liquids.

When evaluating the advantages of this method as a tool for multielemental analysis, several key aspects emerge. Firstly, the ability to simultaneously detect and quantify lead and cadmium represents a significant advancement, simplifying the analytical process by enabling multielement determination in a single run, thereby optimizing laboratory resources and time.

Secondly, the enhanced sensitivity of this method enables the detection of extremely low concentrations of lead and cadmium—critical in scenarios where trace-level presence of these metals may have significant environmental or health implications. The improved selectivity achieved through electrode modification with hydroxyapatite helps minimize interference from other ions in the sample, ensuring more accurate and reliable results.

Therefore, the combination of square-wave stripping voltammetry with a hydroxyapatite-ionic liquid modified sensor for simultaneous ultra-trace determination of lead and cadmium represents a significant advancement in multielemental analytical chemistry.

Challenges of Electrochemical Techniques

Despite their multiple advantages, electrochemical methods also confront various challenges and limitations that must be addressed for effective heavy metal determination. One challenge lies in the stability of the electrodes used in electrochemical measurements. Electrode degradation or fouling can result from factors such as adsorption of unwanted species on the surface or material corrosion, which may compromise result accuracy and reproducibility.

Additionally, coexisting species in the sample may cause interferences that affect the electrochemical response of the target heavy metals. These interferences can be particularly problematic in complex matrices—such as environmental or biological samples—where multiple components may interact with the electrode and generate nonspecific signals. Identifying and mitigating these interferences is essential to ensure selectivity and reliability in heavy metal determination.

Optimizing experimental conditions is another significant challenge when applying electrochemical techniques. The selection of parameters such as applied potential, scan rate, and electrolyte composition can greatly influence method sensitivity and selectivity. However, finding the optimal balance often requires trial and error, as well as technical expertise in instrument operation and data interpretation.

Moreover, validating electrochemical methods can be time-consuming and resource-intensive. Calibration and verification studies are needed to assess accuracy, precision, linearity, robustness, and stability of results under varying experimental conditions and sample characteristics. This process is fundamental to ensure result reliability and validity, as well as analytical reproducibility over time. Nevertheless, this factor tends to improve with experience and the analyst's versatility.

CONCLUSION

Advances in electrochemical research have revealed the promising potential of these techniques for multielemental determination of heavy metals, combining high sensitivity and selectivity. Although traditional methods remain widely used, a future where electrochemical approaches become essential tools for environmental monitoring and toxicological studies is foreseeable.

To realize this potential, it is crucial to address remaining challenges such as optimizing selective electrodes, miniaturizing equipment, and standardizing analytical procedures. These aspects are key to ensuring accuracy and reproducibility of results obtained using electrochemical methods for heavy metal determination.

Ultimately, voltammetry and other electrochemical techniques represent valuable tools for heavy metal detection. Their simplicity, affordability, real-time monitoring capability, and exceptional sensitivity and selectivity position them as indispensable in scientific research, environmental management, and public health protection. With ongoing technological advancement and broader applications across diverse domains, these methods are expected to play an increasingly critical role in detection and evaluation of heavy metal contamination in the future.

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