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Review Article

Metal Detecting Sensors: A Review on the Transition from Traditional Sensors to Field-Portable Sensors

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ABSTRACT

Recently, in-situ analyses have been required in a variety of situations for clinical, food, environmental, and industrial samples. Therefore, not only do devices have to be miniaturized, lightweight, affordable, portable, autonomous, reusable, or disposable, but the approaches used must also be straightforward to understand, friendly, and sensitive enough to yield exact and accurate findings. Electroanalytical chemistry concepts have an advantage over other approaches in that they provide inexpensive and efficient ways to handle them. Thus, it is essential for satisfying the continually changing needs of scientific and industrial research. In this review, the use of these electrochemical methods in metal analysis, particularly for toxic metals, and numerous examples that have been described in the literature over the past ten years are discussed. The detail starts with a description of the traditional sensors and is followed by descriptions and explanations of various cutting-edge devices that will become well-known field-portable sensors during this time.

Keywords: Heavy metals, Toxic metals, Electrochemical detection, Traditional sensor, Portable

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Introduction

From the past to the present, many metals have been employed in the industry to create various products, including mechanical parts, buildings, and jewelry. Besides their benefits, the toxicological effects of metals on both human health and the environment are a delicate issue. With industrial, agricultural, residential, and agricultural waste, as well as transportation, as key sources, metals are easily transported by water, soil, and sediment. This might happen as a result of leaching, atmospheric fallout, or even direct emissions. Sometimes, metals of interest are referred to as "heavy metals," a term that can cover a wide range of metals based on their density, atomic number, atomic weight, chemical composition, or toxicity. Even though the same metals are also referred to as "trace elements" or "trace metals/metalloids". The environmental community is most interested in arsenic, beryllium, barium, cadmium, chromium, copper, mercury, nickel, lead, selenium, vanadium, and zinc [1].

There are several analytical techniques that are frequently used for metal analysis, including atomic spectroscopy, X-ray fluorescence, and inductively coupled plasma mass spectrometry (ICP-MS), as well as theory and equipment [2]. These are routinely utilized for a variety of samples and offer great accuracy when conducted in centralized lab facilities. They, however, call on resources like infrastructure, time, and labor. Only experts with specific knowledge can give reliable results, and uncontaminated samples must be preserved and transported. Storage containers must also be thoroughly inspected to avoid erroneous metal concentrations in samples.

Among these methods, electroanalysis is frequently employed in metal applications. They offer distinctive characteristics. High sensitivity, high selectivity, rapid response, low volume solution requirement, and straightforward operation are of some their advantages. Moreover, the electroanalytical methods can produce accurate and sensitive results without any pretreatment, which lowers the cost of analysis [3]. In contrast to other analytical methods such as atomic absorption spectroscopy (AAS), atomic emission spectroscopy (AES), and inductively coupled plasma (ICP), which calls for intricate and exact pretreatment processes.

Recently, the technology of field portable equipment has advanced quickly, expanding the uses of these instruments in the processing of clinical, food, environmental, and industrial sample data. These devices provide cost-effective, non-destructive, on-site testing of a broad spectrum of inorganic and organic analytes in samples. Moreover, some of them do not even require the use of reagents or produce any waste throughout the analysis procedure. These requirements lead the electroanalytical methods to have numerous growths in research development because the most important potential benefit of electrochemistry is the easy design and fabrication of small-sized sensors. It was found that demand for eco-friendly and affordable materials to produce new electrochemical sensors has grown very fast over time. The development of analytical devices, which is made possible by the possibility of getting trustworthy sensors on a large scale and at an affordable price with adequate performance, is challenging. This review investigates and discusses recent developments in electrochemical techniques, electrode materials, and electrode manufacturing, which start with the traditional electrochemical sensor and evolve into a new generation of portable electrochemical sensors for the on-site detection of toxic metals.

Traditional electrochemical sensors

The analysis of metal ions in environmental samples is crucial for assessing the safety of food, water, and soil. Electrochemical sensors have appeared as a powerful tool for detecting and quantifying metal ions due to their high sensitivity, selectivity, and accuracy. The history of electrochemical sensors dates to the early 19th century when Alessandro Volta discovered the phenomenon of electrochemical cells. The first electrochemical sensor was developed in 1992 by the Hungarian chemist Jaroslav Heyrovsky, who invented the polarography technique. This technique was used for the determination of trace metals in various solutions. Later, the development of the glassy carbon electrode by Fritz Scholz in 1975 led to significant advances in the field of electroanalytical chemistry [4]. To enable the electrochemical reaction to take place, the measurement is carried out in an electrolytic cell using an external power source as a potential generator. This cell consists of a three-electrode arrangement submerged in a supporting electrolyte. A working electrode, where the electrochemical reaction takes place, a reference electrode, whose potential stays constant and is unaffected by the flow of current, and a counter electrode, which completes the circuit, make up the three-electrode system. After applying a potential to a cell, a current that is proportional to the amount of analyte flows between the working electrode and the counter electrode. Figure 1 depicts the elements of an electrochemical cell used in voltammetry.

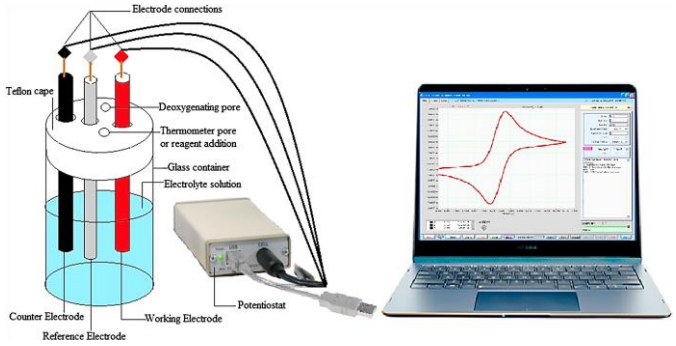

Figure 1 The typical composition of an electrochemical cell used in voltammetry.

Based on the construction of an electrochemical cell, the selection of working electrode materials plays a critical role in the accuracy and sensitivity of the analysis. The classical electrochemistry experiment uses a macro electrode, whose dimensions are greater than 100 μm. The commercial working electrode is typically produced from glassy carbon, stainless steel, carbon paste, platinum, and gold. Among these materials, glassy carbon electrode (GCE) [5] is widely used for metal analysis due to its high chemical stability, low background current, and wide potential window. GCE has been extensively employed to determine various metal ions in environmental samples, including wastewater, tap water, and soil samples. Stainless steel electrode (SSE) [6] is a cost-effective and widely available electrode that has been utilized for the determination of metal ions in samples such as industrial wastewater and

soil. Carbon paste electrode (CPE) [7] is a versatile electrode that can be easily modified with various materials to enhance its sensitivity and selectivity for metal ion analysis in environmental samples. CPE has been used for the determination of metal ions in samples such as lake water and human serum. Gold electrode (AuE) [8] is a highly sensitive electrode that has been extensively used for the determination of trace metal ions in environmental samples. Due to its excellent conductivity and chemical stability, AuE has been employed for the determination of metal ions in samples such as milk and lettuce.

The traditional electrochemical sensors for the measurement of heavy metal ions from 2013 to 2023 are listed in Table 1. The details cover the specifics of electrode materials, target analytes, methodologies, analytical performances, and real samples. Besides the choice of electrode material, the selection of appropriate techniques is another key factor that directly affects accuracy. Several electrochemical techniques, including cyclic voltammetry, linear sweep voltammetry, differential pulse voltammetry, square wave voltammetry, and electrochemical impedance spectroscopy [8], have been developed for the analysis of metal ions. Based on the use of the mentioned working electrode materials, here is a detailed description of popular techniques used for metal analysis and some examples of publications.

Differential pulse anodic voltammetry (DPAV) [9] is a widely used technique for the determination of metal ions in environmental samples because this technique provides high sensitivity. DPAV involves applying a potential to the working electrode and measuring the resulting current. The potential is scanned over a range of values, and the resulting current is recorded. The difference between the peak current and the background current is then used to determine the concentration of the metal ion. For example, Zhang et al. [10] reported on the use of modified glassy carbon electrodes by NH_2-ssDNA-grafted reduced graphene oxide (RGO) for Hg(II) detection in synthetic samples. The sensor provided a low limit of detection at 5 nM and a wide concentration range (8–100 nM). Ting et al. [11] synthesized the composite of graphene quantum dots (GQDs) and gold nanoparticles (AuNPs) for high-response detection of Hg(II) and Cu(II) ions. They found that their modified electrode has a very high sensitivity with a low limit of detection. Veerakumar et al. [12] fabricated a selective and sensitive electrochemical sensor for the detection of toxic metal ions (Cd(II), Pb(II), Cu(II), and Hg(II)) using a GCE modified with a composite of palladium nanoparticles (PdNPs) on porous activated carbons (PACs). It was found that the detectable concentrations are down to 41 nM, 50 nM, 66 nM, and 54 nM, for Cd(II), Pb(II), Cu(II), and Hg(II), respectively.

Differential pulse anodic stripping voltammetry (DPASV) is a highly sensitive electroanalytical technique that involves the deposition of metal ions onto the working electrode, followed by stripping the metal ions off the electrode by applying a positive potential. For example, Muralikrishna et al. [13] modified GCE by reducing and functionalizing graphene oxide with L-cysteine (L-cys-rGO) for simultaneous quantification of environmentally hazardous metal ions such as Cd(II), Pb(II), Cu(II), and Hg(II) by DPASV as presented in Figure 2A. This modified sensor can detect heavy metal ions in environmental and industrial samples, with a low limit of detection for Cd(II) of 3.26 nM, Pb(II) of 3.31 nM, Cu(II) of 4.12 nM, and Hg(II) of 5.50 nM. This sensor was applied for quality control analysis

of water from the environment and industry. Guo et al. [14] used reduced graphene oxide (RGO) and chitosan (CS) as RGO-CS for coating onto the glassy carbon electrode (GCE) surface and follow by coating with poly-L-lysine films (PLL). This proposed sensor can be used to perform simultaneous electrochemical determination of heavy metal ions Cd(II), Pb(II), and Cu(II) by DPASV in a tap water sample with acetate buffer (0.1 mol/L, pH 4.5) as a supporting electrolyte. As a result, this sensor has a wide range of linearity and a low limit of detection that is sufficient for analyzing heavy metal ions in practical applications. As demonstrated in Figure 2B, Lu et al. [15] prepared MOFs by composite synthetization via the in-situ growth of the UiO-66-NH_2 crystal on the graphene aerogel (GA) matrix. This composite is coated onto the surface of GCE. The modified electrode is sensitive enough to detect heavy metals such as Cd(II), Pb(II), Cu(II), and Hg(II) ions in river water and leaching solutions from soil and vegetables. This developed sensor provides a wide linearity range (around 5–4000 nM depending on metal ions) and a very low limit of detection at 9 nM, 1 nM, 8 nM, and 0.9 nM, respectively.

Square wave anodic stripping voltammetry (SWASV) [16] is a highly sensitive electroanalytical technique similar to DPASV but involves applying a square wave potential to the working electrode. SWASV has been shown to be more sensitive than DPASV for the determination of some metal ions due to the optimization of the waveform parameters. For instance, Afkhami et al. [17] used N, N′-bis(3-(2-thenylidenimino)propyl) piperazine-coated silica nanoparticles (L-MSNPs) modified carbon paste electrodes (CPE) to simultaneously detect heavy metal ions including Cd(II), Cu(II), and Hg(II) in artificial samples with an incredibly high level of sensitivity. In accordance with the experiment results, this modified sensor is particularly appropriate for analyzing heavy metal ions due to its great linearity and low detection limit within practical applications. Lin et al. [18] described the use of laser etching of polyimide (PI) sheets to produce graphene-based carbon nanomaterials (LEGCNs) modified GCE for simultaneous detection of Cd(II) and Pb(II). This electrode provided a large specific surface and numerous edge-plane active sites, which facilitate the accumulation of metal ions. The performance of this modified electrode shows a great low limit of detection that is sufficient for the analysis of heavy metal ions reported by the World Health Organization (WHO) [19]. In particular, the proposed electrode exhibits remarkable repeatability, reproducibility, selectivity, and stability. And the last work of this technique, Abdelaziz et al. [20] reported on the use of modified CPE with aluminum oxide nanoparticles (NP-Al_2O_3) for the analysis of lead, Pb (II), and mercury, Hg(II) simultaneously. From its analytical performance, it is clear that this sensor has a large concentration range for analysis at low concentrations of Pb(II) and Hg(II) at 0.76 nM and 0.50 nM, respectively. Lastly, this developed sensor has a lot of performance for the analysis of multiple heavy metal ions in tap water samples.

Electrochemical impedance spectroscopy (EIS) [21] is a powerful technique that has gained attention for the analysis of metal ions. EIS involves the application of an AC potential to the working electrode, and the resulting current is measured. By varying the amplitude and frequency of the potential, the resulting data can be analyzed to determine the impedance of the electrode at different frequencies. This information is valuable as it provides insight into the electrochemical properties of the electrode,

including its resistance and capacitance. It can be used to determine the concentration of metal ions in environmental samples. EIS has been successfully used to determine metal ions in various environmental samples, including groundwater, wastewater, and sediment samples. Wei et al. [22] have developed an electrochemical sensor for detecting Cr(VI) in drinking water using electrochemical impedance spectroscopy. The method is based on the specific binding of crown ethers to $HCrO_4^-$, which forms sandwich complexes between them via hydrogen bonds and moiety interactions with K^+ captured by azacrown on its self-assembled Au electrode surface. This crown ether blocks the access of redox probes to the self-assembled Au electrode, increasing the electron transfer resistance. The obtained detection limit of 0.054 nM from this sensor is much lower than the drinking water safe limit prescribed by the U.S. EPA. In addition, the azacrown self-assembled Au electrode has good selectivity for Cr(VI) with good stability and low interferences. Chen et al. [23] presented the development of a label-free biosensor that can detect three different targets, namely Hg(II), adenosine triphosphate (ATP), and thrombin, but in this review, we focus on mercury ions; Hg(II). They used DNA with T-T mismatch to recognize Hg(II) and form a T-Hg(II)-T complex, resulting in a decreased charge transfer resistance (R_{ct}). The biosensor can selectively detect Hg(II) with a detection limit of 0.03 nM. The biosensor has potential applications in practical detection and can be used in various fields, including environmental monitoring, clinical diagnosis, and food safety.

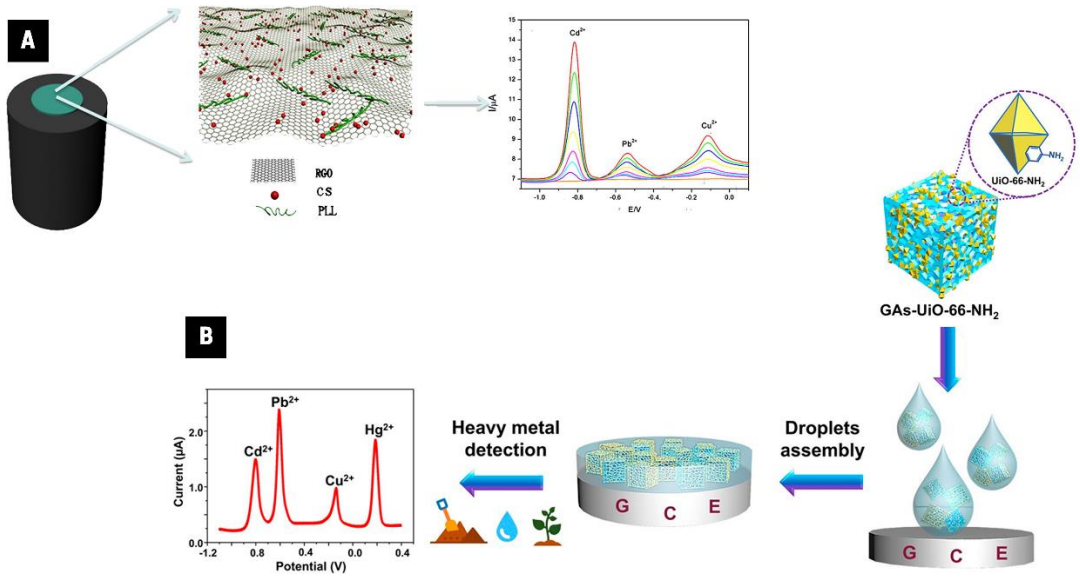

Figure 2 (A) Schematic illustration of RGO-CS/PLL/GCE for trace Cd(II), Pb(II), and Cu(II). Reprint from Ref. [14] Guo Z, Li D-d, Luo X-k, Li Y-h, Zhao Q-N, Li M-m, et al. Simultaneous determination of trace Cd(II), Pb(II), and Cu(II) by differential pulse anodic stripping voltammetry using a reduced graphene oxide-chitosan/poly-l-lysine nanocomposite modified glassy carbon electrode. J Colloid Interface Sci. 2017; 490:11-22. (B) Schematic illustration of the UiO-66-NH_2 crystal on gas matrix and the detection of heavy-metal ions by GAs-UiO-66-NH_2 modified electrode. Reprint from Ref. [15] Lu

M, Deng Y, Luo Y, Lv J, Li T, Xu J, et al. Graphene aerogel–metal–organic framework-based electrochemical method for simultaneous detection of multiple heavy-metal ions. Anal Chem. 2019;91(1):888-95.

Table 1 The conclusion of traditional electrochemical sensors for analysis of heavy metal ions.

Electrode	Modifier	Metal ion	Linearity (nM)	Technique	LOD (nM)	Sample	Ref.
GCE	NH_2-ssDNA-grafted reduced graphene oxide (RGO)	Hg(II)	8 - 100	DPAV	5.00	synthetic samples	[10]
GCE	Ion-imprinted polymeric nanobeads (IIP) and multi-wall carbon nanotubes (MWCNTs)	Hg(II)	10 - $7x10^5$	DPASV	5.00	ground and wastewater samples	[24]
GCE	Amine-Fe_3O_4 nanoparticles	Pb(II)	500 - 8000	SWASV	4.36	wastewater	[25]
CPE	N,N′-bis(3-(2-thenylidenimino) propyl)piperazine coated silica nanoparticles (L-MSNPs-CPE)	Cd(II) Cu(II) Hg(II)	Cd(II) 80.2 - 535 Cu(II) 56.7 - 10400 Hg(II) 15 - 3000	SWASV	Cd(II) 15.99 Cu(II) 9.47 Hg(II) 1.50	synthetic samples	[17]
GCE	Reduce graphene oxide with L-cysteine (L-cys-rGO)	Cd(II) Pb(II) Cu(II) Hg(II)	400 - 2000	DPASV	Cd(II) 3.26 Pb(II) 3.31 Cu(II) 4.12 Hg(II) 5.55	environmental samples and industrial samples	[13]
Titania nanotube arrays	Au nanoparticules	Cr(VI)	100 - 10500	Amp	30	tap and lake water samples	[26]

Electrode	Modifier	Metal ion	Linearity (nM)	Technique	LOD (nM)	Sample	Ref.
GCE	Nitrogen-doped microporous carbon/nafion/bismuth-film	Cd(II) Pb(II)	Cd(II) 17.81 - 89.05 and 89.05 - 890.5 Pb(II) 2.41 - 48.20 and 48.20 - 482.0	DPASV	Cd(II) 13.36 Pb(II) 0.120	aqueous samples	[27]
GCE	Gold nanoparticle-graphene-cysteine composite (Au-GN-Cys)	Cd(II) Pb(II)	Cd(II) 40 - 320 Pb(II) 6.05 - 484	SWASV	Cd(II) 0.89 Pb(II) 0.24	aqueous samples	[28]
GCE	Graphene-MWCNTs nanocomposites and Nafion (GO/MWCNTs/Nafion)	Cd(II) Pb(II)	Cd(II) 2.41 - 144.46 Pb(II) 4.45 - 266.97	DPASV	Cd(II) 0.96 Pb(II) 2.67	real water samples	[29]
AuE	6-mercapto-1-hexanol (MCH)	Hg(II)	0.05 - 10	EIS	0.03	synthetic samples	[23]
GCE	Graphene quantum dots (GQDs) and gold nanoparticles (AuNPs)	Hg(II) Cu(II)	0.02 -1.5	DPAV	Hg(II) 0.02 Cu(II) 0.05	-	[11]
GCE	Palladium nanoparticles (PdNPs) on porous activated carbons (PACs)	Cd(II) Pb(II) Cu(II) Hg(II)	Cd(II) 50 - 550 Pb(II) 50 - 890 Cu(II) 50 - 500 Hg(II) 24 - 750	DPAV	Cd(II) 41 Pb(II) 50 Cu(II) 66 Hg(II) 54	milk sample	[12]
GCE	Ionic liquid, graphene, and phosphorus ylide	Tl(I) Pb(II) Hg(II)	Tl(I) 10 - 1000 Pb(II) 5 - 1000 Hg(II) 2 - 1000	DPASV	Tl(I) 5 Pb(II) 3 Hg(II) 2	tap water, river water, and soil samples	[30]
CPE	Reduced graphene oxide/gold nanoparticle (RGO/AuNPs)	Hg(II)	5 - 840	DPASV	2.04	soil samples	[31]
AuE	Azacrown, $HCrO_4^-$, K^+	Cr(IV)	19.23 - 1923.3	EIS	0.054	drinking water	[22]

Electrode	Modifier	Metal ion	Linearity (nM)	Technique	LOD (nM)	Sample	Ref.
GCE	Carboimidazole grafted reduced graphene oxide (RGO-NH-Ci)	Hg(II) Pb(II)	Hg(II) 0.6 - 10 and 10 - 9000 Pb(II) 5 - 1200 and 1200 - 10000	DPASV	Hg(II) 0.2 Pb(II) 3.0	real water sample	[32]
GCE	Fe_2O_3/graphene/bismuth nanocomposite	Zn(II) Cd(II) Pb(II)	Zn(II) 15.30 - 1530.40 Cd(II) 8.90 - 889.90 Pb(II) 4.83 - 482.70	DPASV	Zn(II) 1.68 Cd(II) 0.61 Pb(II) 0.34	tap water and river water samples	[33]
GCE	Polyaniline (PA) functionalized with polypyrrole/graphene oxide (PPy/GO) nanocomposites	Cd(II) Pb(II)	Cd(II) 0.45 - 447.60 Pb(II) 0.24 - 482.70	DPAV	Cd(II) 0.44 Pb(II) 0.14	tap water samples	[34]
GCE	A fluorescent (Pi-A) immobilized on a reduced graphene oxide (RGO) surface (Pi-A/RGO) nanocomposite	Cu(II)	78.61 - 4686	SWASV	10.54	tap and lake water sample	[35]
GCE	1-(2, 4-dinitrophenyl)-dodecanoylthiourea (DAN)	Hg(II)	9.99 - 109.90	DPASV	3.19	tap and drinking water	[36]
GCE	Thymine modified gold nanoparticles/reduced graphene oxide (AuNPs/rGO) nanocomposites	Hg(II)	0.05 - 499	DPAV	0.00747	tap water	[37]
GCE	Thiol and amino-functionalized porous Si nanowires (Si NWs-NH_2)	Cd(II) Pb(II)	Cd(II) 5 - 250 Pb(II) 5 - 250	SWASV	-	-	[38]

Electrode	Modifier	Metal ion	Linearity (nM)	Technique	LOD (nM)	Sample	Ref.
GCE	Thymine-rich, single-stranded DNA (ssDNA) and mesoporous carbon (OMC) and self-doped polyaniline (SPAN) nanofibers (DNA/ AuNPs/OMC/SPAN/GCE)	Hg(II)	0.01 - 1000	DPAV	0.00	sediment pore water and tap water	[39]
GCE	Alkalization-intercalated Ti_3C_2 (alk-Ti_3C_2)	Cd(II) Pb(II) Cu(II) Hg(II)	100 - 1500	SWASV	Cd(II) 98 Pb(II) 41 Cu(II) 32 Hg(II) 130	-	[40]
Indium tin oxide (ITO)	Co_3O_4 nanosheets	Pb(II)	4.83 - 483	DPASV	2.51	tap water	[41]
GCE	Polypyrrole-graphene (PPY-rGO) nanocomposite	Pb(II)	5 - 750	SWASV	0.05	tap water	[42]
GCE	DNA-modified Fe3O4@Au magnetic nanoparticles (NPs)	Ag(I) Hg(II)	Ag(I) 10 - 150 Hg(II) 10 - 100	SWASV	Ag(I) 3.4 Hg(II) 1.7	real water sample	[43]
GCE	Reduced graphene oxide (RGO) and Chitosan (CS) (RGO-CS) and poly-L-lysine films (PLL)	Cd(II) Pb(II) Cu(II)	Cd(II) 0.44 - 89.00 Pb(II) 0.24 - 48.19 Cu(II) 0.79 - 157.48	DPASV	Cd(II) 0.09 Pb(II) 0.10 Cu(II) 0.32	tap water sample	[14]
GCE	Bismuth film and polyimide (PI) sheets laser etched graphene (LEGCNs)	Cd(II) Pb(II)	Cd(II) 62.27 - 1067.52 Pb(II) 24.14 - 578.27	SWASV	Cd(II) 4.18 Pb(II) 1.98	lake water samples	[18]

Electrode	Modifier	Metal ion	Linearity (nM)	Technique	LOD (nM)	Sample	Ref.
Stainless steel (SS)	Ethylenediaminetetraacetic acid (EDTA) chelating ligand and modified polyaniline (PANI) and single-walled carbon nanotubes (SWCNTs); EDTA_PANI/SWCNTs	Cu(II) Pb(II) Hg(II)	Cu(II) 1200 - $2x10^6$ Pb(II) 2000 - $37x10^3$ Hg(II) 200 - $2x10^6$	DPAV	Cu(II) 80 Pb(II) 1650 Hg(II) 680	-	[44]
ZnO nanorods	(ZnO/reduced graphene oxide (rGO) Schottky barrier and polypyrrole (PPy)	Hg(II)	2 - 10	DPAV	1.90	sea water	[45]
Stainless steel (SS)	EDTA-Ppy (polypyrrole) /SWNTs (single-walled carbon nanotubes) nanocomposite	Pb(II)	150 - 800000	DPAV	70	-	[46]
GCE	blast furnace slag (BFS)	Pb(II)	1000 - 5000	DPAV	15	-	[47]
GCE	Graphene Aerogel–Metal-Organic Framework	Cd(II) Pb(II) Cu(II) Hg(II)	Cd(II) 60 - 3000 Pb(II) 10 - 4000 Cu(II) 100 - 3500 Hg(II) 5 – 3000	DPASV	Cd(II) 9 Pb(II) 1 Cu(II) 8 Hg(II) 0.9	river water and the leaching solutions of soil and vegetable	[15]
CPE	NP-Al_2O_3 powder	Pb(II) Hg(II)	Pb(II) 3000 - 21000 Hg(II) 3000 - 21000	SWASV	Pb(II) 0.76 Hg(II) 0.50	tap water	[20]
GCE	Bioextract decorated with functionalized carbon nanotubes (BioExt/MWCNTs)	Cd(II)	50 - 6000	DPASV	1.01	river and drinking water	[48]

Electrode	Modifier	Metal ion	Linearity (nM)	Technique	LOD (nM)	Sample	Ref.
GCE	Metal-organic framework (MOF) hexagonal lanthanide MOF, ZJU-27 prepared $Yb(NO_3)_3 \cdot 5H_2O$ with 1,3,5-benzenetrisbenzoic acid (H3BTB) in the presence of 2-FBA	Cd(II) Pb(II)	Cd(II) 100 - 1000 Pb(II) 100 - 1000	SWASV	Cd(II) 2.03 Pb(II) 1.10	real water sample	[49]
GCE	SnS-decorated Bi_2O_3 nanosheets heterostructure	Cd(II) Pb(II)	Cd(II) 100 - 1000 Pb(II) 100 - 1000	SWASV	Cd(II) 1.50 Pb(II) 1.40	tap water and lake water	[50]
GCE	Bismuth-nanoparticle (BiNPs) onto $Ti_3C_2T_x$ sheets	Cd(II) Pb(II)	Cd(II) 80 - 800 Pb(II) 60 - 600	SWASV	Cd(II) 12.4 Pb(II) 10.8	tap and lake water	[51]
GCE	Polyaniline, ZrO_2-SO_4^{2-} and multi-walled carbon nanotubes (MWCNT) nanostructures	Cr(IV)	55 - 13700 and 13700 - 39500	DPASV	64.33	wastewater from the industrial barium chromate production line	[52]
GCE	Metal-organic framework material UiO-66 and Bi co-deposited (CUiO-66/Bi))	Cd(II) Pb(II)	Cd(II) 89.06 - 445.31 Pb(II) 48.24 - 241.22	SWASV	Cd(II) 0.01 Pb(II) 5.50	tap water and river water	[53]
GCE	Carbon disulfide-functionalized graphene oxide (GOCS) and cadmium ion-imprinted polymer (IIP): CS_2: GO	Cd(II)	4.45 - 444.98	DPCSV	2.05	lettuce, orange, and peach	[54]

GCE = glassy carbon electrode, AuE = gold electrode, ZnO = zinc oxide, Amp = amperometry, DPASV = differential pulse anodic stripping voltammetry, DPCSV = differential pulse cathodic stripping voltammetry, SWASV = square wave anodic stripping voltammetry

Even though the traditional electrochemical sensors offer several advantages for analyzing metal ions in environmental samples, including their sensitivity and selectivity, which allow for the detection and quantification of metal ions at low concentrations, they still have some drawbacks. To be highlighted here, the traditional electrochemical sensors are not suitable for on-site analysis, particularly for a strict timeframe of analysis. For example, quantify the levels of chemical contamination on-site in drinking water and the amount of metal in plating, allowing them to make prompt interventions. Therefore, the creation of a new generation of portable electrochemical sensors geared towards trace-level in-situ metal sensors is a challenge with the potential to be the foundation of new sensors.

Portable electrochemical sensor

Portable electrochemical sensors have emerged as a reliable and efficient analytical technique for detecting and quantifying metal ions in environmental samples. Among them, screen-printed electrodes have gained popularity due to their numerous advantages over traditional methods. Screen-printed electrodes are created by printing conductive ink, such as carbon, graphene, or gold, onto a substrate, such as ceramic or plastic. This process enables the development of miniaturized and portable sensors that are highly sensitive and selective toward metal ion detection. These sensors are also cost-effective, making them an attractive option for environmental monitoring.

Electrochemical techniques, such as SWV, DPV, and amperometry, have been extensively employed with screen-printed electrodes for metal ion analysis due to their high sensitivity, selectivity, and rapid response times. Despite using portable electrochemical sensors, these techniques still operate similarly to traditional methods, ensuring reliable and accurate results. Electrochemical techniques with portable and screen-printed electrodes have revolutionized metal ion analysis, allowing for reliable and accurate results in real-time analysis, even in complex matrices. As more efficient and reliable portable electrochemical sensors are developed, their significance in environmental monitoring and analysis is expected to grow. This section will discuss the importance of analyzing metal ions in samples, the role of portable and screen-printed electrodes in metal ion analysis, and the significance of electrochemical techniques for detecting metal ions.

Screen-printed electrodes can be easily integrated into portable electrochemical sensors, which can be used for on-site and real-time monitoring of metal ions in environmental samples. The small size of screen-printed electrodes also reduces the number of samples required for analysis, making them suitable for analyzing metal ions in complex matrices. This electrode is particularly important in environmental samples and so on, where the presence of multiple contaminants can interfere with the analysis of metal ions.

Therefore, the analysis of metal ions in environmental samples is crucial for protecting human health and the ecosystem. Portable electrochemical sensors, particularly screen-printed electrodes, have gained significant attention in recent years due to their portability, low cost, and high sensitivity and selectivity

toward metal ion detection. Electrochemical techniques, such as square wave voltammetry (SWV), adsorptive differential pulse voltammetry (AdDPV), differential pulse stripping voltammetry (DPSV), and amperometry techniques, are widely used with screen-printed electrodes for metal ion analysis, offering several advantages over traditional analytical techniques. The development of more efficient and reliable portable electrochemical sensors is expected to play a significant role in environmental monitoring and analysis. To make it simpler to comprehend. This section reviews studies based on the kind of material that is utilized as a sensor.

1. Screen-printed carbon electrode

Screen-printed carbon electrodes (SPCE) have become increasingly important in the analysis of metal ions in environmental samples due to their portability, low cost, and high sensitivity and selectivity. These electrodes are fabricated by printing carbon ink onto a substrate, such as ceramic or plastic, and offer several advantages over traditional analytical techniques, including rapid response times and minimal sample preparation. The use of SPCE has also led to the development of miniaturized and portable sensors, which can be used for on-site and real-time monitoring of metal ions. In recent years, SPCE has gained significant attention in the analysis of metal ions due to their high sensitivity and selectivity Figure 3. The electrochemical techniques used with SPCEs, such as SWV, AdDPV, DPSV, and amperometry techniques, have also contributed to the popularity of SPCE in metal ion analysis.

This review will provide an overview of the current state of research on SPCE for metal ion analysis, including their fabrication and properties, the electrochemical techniques used with SPCE, and their applications of SPCEs in environmental monitoring. This review aims to provide a comprehensive understanding of the potential of SPCE for the analysis of metal ions in environmental samples and to highlight the challenges and opportunities in this field. In the following sections, we will discuss the fabrication and properties of SPCE, the electrochemical techniques used with SPCE for metal ion analysis, and the applications of SPCE in environmental monitoring.

Figure 3 Schematic illustration for preparation of SIM/SPCE and application for analysis of Cd^{2+}, Pb^{2+}, Cu^{2+}, and Hg^{2+}. Reprint from Ref. [85] Lv H, Zhang G, Yang W, Dai X, Huang Y, Ni J, et al. Portable anti-fouling electrochemical sensor for soil heavy metal ions detection based on the screen-printed carbon electrode modified with silica isoporous membrane. J Electroanal Chem. 2023;930:117141.

Table 2 The conclusion of portable electrochemical sensors in part of screen-printed carbon electrode for analysis of heavy metal ions.

Electrode	Modifier	Metal ion	Linearity (nM)	Technique	LOD (nM)	Sample	Ref.
SPCE	Polypyrrole/carbonaceous nanospheres (PPy/CNSs)	Hg(II) Pb(II)	Hg(II) 5 - 35 Pb(II) 1 - 7	SWASV	Hg(II) 0.021 Pb(II) 0.004	river water	[55]
SPCE	Fe_3O_4 microspheres and room temperature ionic liquid (RTIL) (Fe_3O_4-RTIL)	As(III)	13.34 - 133.4	SWASV	0.01	water	[56]
SPCE	Bismuth film and DMG (adsorptive reagent)	Pd(II) Pt(II) Rh(II)	Pd(II) 24.06 - 48.58 Pt(II) 2.10 - 3.64 Rh(II) 1.36 - 3.69	AdDPSV	Pd(II) 0.075 Pt(II) 0.0003 Rh(II) 0.049	water	[57]
SPCE	Lead film (PbF) and DMG (adsorptive reagent)	Co(II) Ni(II)	Co(II) 10.16 - 100.12 Ni(II) 10.22 - 49.38	SWAdSV	Co(II) 3.34 Ni(II) 5.11	snow water	[58]
SPCE	Bi and potassium ferricyanide	Pb(II) Cd(II)	Pb(II) 24 - 724 nM Cd(II) 44.48 - 1334.4	SWASV	Pb(II) 0.001 Cd(II) 0.25	dust	[59]
SPCE	Graphene/polyaniline/polystyrene (G/PANI/PS) nanoporous fiber	Pb(II) Cd(II)	Pb(II) 0.05 - 2410 Cd(II) 0.09 - 4450	SWASV	Pb(II) 0.02 Cd(II) 0.04	river water	[60]
SPCE	In-situ antimony	Cd(II) Pb(II) Cu(II)	Cd(II) 55.11 - 644 Pb(II) 63.6 - 302.0 Cu(II) 83.5 - 1573.0	DPASV	Cd(II) 30.26 Pb(II) 24.10 Cu(II) 25.20	ground water	[61]
SPCE	Bismuth	Ni(II) Co(II)	Ni(II) 17 - 170 Co(II) 84.84 - 848.40	AdCSV	Ni(II) 0.46 Co(II) 1.59	sewer water	[62]
SPCE	Graphene–polyaniline (G/PANI) nanocomposite	Zn(II) Cd(II) Pb(II)	Zn(II) 15.3 - 4588.5 Cd(II) 8.90 - 2668.8 Pb(II) 5 - 1448	SWASV	Zn(II) 15.3 Cd(II) 0.89 Pb(II) 5.00	human serum	[63]

Electrode	Modifier	Metal ion	Linearity (nM)	Technique	LOD (nM)	Sample	Ref.
SPCE	Bismuth film/Nafion/ionic liquid/graphene composite (BiF/N/IL/G)	Zn(II) Cd(II) Pb(II)	Zn(II) 1.53 - 1528 Cd(II) 0.89 - 891 Pb(II) 0.48 - 482	SWASV	Zn(II) 1.38 Cd(II) 0.53 Pb(II) 0.39	water	[64]
SPCE	Glutathione-aryl diazonium electrochemical grafting (GSH)	Cd(II) Pb(II)	Cd(II) 96.1 - 1340 Pb(II) 48.79 - 724.70	DPASV	Cd(II) 28.50 Pb(II) 14.48	waste water	[65]
SPCE	Au	Hg(II)	4.99 - 499.1	SWASV	4.99	ground water	[66]
SPCE	Ex-situ bismuth and quercetin -50-sulfonic acid	Sb(III)	22.15 - 369.70	AdDPSV	6.57	ground water	[67]
SPCE	Graphene-modified screen-printed electrode (SPCE-GPH) Carbon nano-fibers modified screen-printed electrodes (SPCE-CNF) Multi-walled carbon nanotubes modified screen-printed electrode (SPCE-MWCNT)	Cd(II) Pb(II)	Cd(II) 117.4 - 892.27 (GPH) 32.91 - 892.27 (CNF) 76.51- 892.27 (MWCNT) Pb(II) 138.9 - 489.11 (GPH) 33.34 - 489.11 (CNF) 70.93 - 489.11 (MWCNT)	DPASV	Cd(II) 35.60 (GPH) 9.79 (CNF) 23.10 (MWCNT) Pb(II) 41.48 (GPH) 10.12 (CNF) 21.19 (MWCNT)	water	[68]
SPCE	Polystyrene sulfonate (PSS) and carbon nanopowder (CnP)	Cd(II) Pb(II)	Cd(II) 4.5 - 450 Pb(II) 2.4 - 480	DPASV	Cd(II) 90 Pb(II) 1.3	water	[69]
SPCE	Antimony film and DMG (chelating reagent)	Pb(II)	4.83 - 483.10	AdSV	13.02	tap water	[70]

Electrode	Modifier	Metal ion	Linearity (nM)	Technique	LOD (nM)	Sample	Ref.
SPCE	Calixarene bulk	Pb(II) Cu(II) Hg(II)	Pb(II) 482.70 - 11590 Cu(II) 1575 - 37820 Hg(II) 499 - 11980	DPASV	Pb(II) 183.4 Cu(II) 629.7 Hg(II) 239.3	industrial and environmental water	[71]
SPCE	-	Pb(II)	$3x10^3$ - $1.34x10^5$	DPASV	$1.32x10^3$	soil water and pond water	[72]
SPCE	Antimony-graphene oxide	Cd(II) Pb(II) Cu(II) Hg(II)	100 - 1500	SWASV	Cd(II) 54 Pb(II) 26 Cu(II) 60 Hg(II) 66	sewage, fertilizer waste, and sea water	[73]
SPCE	Bismuth (Bi)) film and gold nanoparticles (AuNPs)	Zn(II) Pb(II) Cu(II)	Zn(II) 15 - 6882 Pb(II) 5 - 2172 Cu(II) 15 - 7080	DPASV	Zn(II) 0.76 Pb(II) 9.65 Cu(II) 0.47	lake water	[74]
SPCE	Gold nanoparticles	Cr(IV)	384.6 - 3846	LSV	103.8	water	[75]
SPCE	ZnO@G nanocomposites	Cd(II) Pb(II)	Cd(II) 89 - 1780 Pb(II) 48 - 965	SWASV	Cd(II) 5.33 Pb(II) 3.86	waste water	[76]
SPCE	Bismuth nanoparticles decorated graphene-carbon nanotubes nanocomposite (BiNPs@Gr-CNTs)	Hg(II)	1.0 - $2.17x10^5$	DPASV	0.2	tap water, fish oil tablets, human serum, and urine	[77]
SPCE	Dimethylglyoxime (DMG)	Ni(II)	130 - 3410	AdSV	40	waste water	[78]
SPCE	Exfoliated bismuthene suspension (2D Bi exf)	Cd(II) Pb(II)	Cd(II) 1.78 - 222.40 Pb(II) 0.97 - 120.48	DPASV	Cd(II) 0.62 Pb(II) 0.29	water	[79]

Electrode	Modifier	Metal ion	Linearity (nM)	Technique	LOD (nM)	Sample	Ref.
SPCE	Gold nanoparticles, polyaniline, and multi-walled carbon nanotubes	Zn(II) Pb(II) Cu(II)	Zn(II) 15.31 - 2752.60 Pb(II) 4.83 - 86.81 Cu(II) 15.73 - 2832.42	SWASV	Zn(II) 0.60 Pb(II) 0.18 Cu(II) 0.27	water	[80]
SPCE	Two-dimensional antimonene-based (2D Sb)	Pb(II) Cd(II)	Pb(II) 5.31 - 618.90 Cd(II) 81 - 1180	DPASV	Pb(II) 1.45 Cd(II) 24.04	water	[81]
SPCE	Schiff Base Ligand	Zn(II)	$1x10^3 - 1x10^8$	LSV	$3.5x10^2$	-	[82]
SPCE	Bimetallic copper-bismuth alloy nanoparticles	Pb(II) Cd(II) Zn(II)	Pb(II) 2.41 - 3377 Cd(II) 44.53 - 8009 Zn(II) 2296 - 9173	SWASV	Pb(II) 0.39 Cd(II) 8.45 Zn(II) 535.2	human biological liquids (blood and urine) and environmental water	[83]
SPCE	-	Fe(III) Cu(II)	Fe(III) 223.5 - 7155 Cu(II) 17.95 - 6294	AdSV	Fe(III) 66.97 Cu(II) 5.35	waste water	[84]
SPCE	Silica isoporous membrane (SIM)	Cd(II) Pb(II) Cu(II) Hg(II)	Cd(II) 200 - 20000 Pb(II) 10 - 10000 Cu(II) 200 - 20000 Hg(II) 10 - 10000	SWASV	Cd(II) 9.3 Pb(II) 1.1 Cu(II) 16.2 Hg(II) 1.4	soil sample	[85]
SPCE	Bismuth powder mixed with carbon ink	Cd(II)	44.5 - 445	SWASV	42.7	water	[86]

Electrode	Modifier	Metal ion	Linearity (nM)	Technique	LOD (nM)	Sample	Ref.
SPCE	a three-dimensional melamine-doped graphene oxide/MXene composite aerogel (3D MGMA)	Zn(II) Cd(II) Pb(II)	Zn(II) 45.9 - 1380 Cd(II) 26.7 - 801 Pb(II) 14.5 - 434	DPASV	Zn(II) 7.34 Cd(II) 3.99 Pb(II) 1.39	tap water and cereal	[87]
SPCE	Butterfly-shaped silver nanostructure (AgNS)	Cd(II) Cu(II) Pb(II) Hg(II)	Cd(II) 44.48 - 2668.80 Cu(II) 786.78 - 7867.82 Pb(II) 24.12 - 433.98 Hg(II) 24.93 - 497.82	DPASV	Cd(II) 3.56 Cu(II) 114.9 Pb(II) 12.06 Hg(II) 3.49	water	[88]

SPCE = screen-printed carbon electrode, DMG = dimethyl glyoxime, ZnO@G = zinc oxide and graphene nanocomposite, SWASV = square wave anodic stripping voltammetry, AdDPSV = adsorptive differential pulse stripping voltammetry, SWAdSV = square wave anodic adsorptive striping voltammetry, AdCSV = adsorptive cathodic stripping voltammetry, AdSV = adsorptive stripping voltammetry, DPASV = differential pulse anodic stripping voltammetry, LSV = linear sweep voltammetry

From Table 2, we will describe the works that are outstanding in terms of novelty or can detect multiple types of heavy metal using electrochemical techniques on a screen-printed carbon electrode (SPCE). Promphet et al. [60] fabricated on a screen-printed carbon electrode (SPCE) using electrospinning of graphene/polyaniline/polystyrene (G/PANI/PS) nanoporous fibers for the simultaneous determination of lead; Pb(II) and cadmium; Cd(II). The developed sensor was used to detect heavy metal ions by square-wave anodic stripping voltammetry (SWASV) in real river water samples containing bismuth; Bi (III). Hence, Bi (III) can form a complex with Pb(II) and Cd(II) ions, enhancing their electrochemical signals and their detection sensitivity. In addition, the use of Bi(III) can reduce interference from other metal ions typically present in environmental water samples. From the experiment of this work, they discovered this sensor has a wide range of concentrations of heavy metal ions (Pb(II) 0.05 – 2410 nM and Cd(II) 0.09 – 4450 nM) and a low limit of detection (Pb(II) 0.02 nM and Cd(II) 0.04 nM) that is enough to analyze Pb(II) and Cd(II) in a real sample. Chaiyo et al. [64] developed a simple, low-cost, and highly sensitive electrochemical sensor for the simultaneous detection of zinc; Zn(II), cadmium; Cd(II), and lead; Pb(II) in water samples. The sensor is based on a Nafion/ionic liquid/graphene composite, modified screen-printed carbon electrode, and is disposable. The electrode demonstrates high conductivity and rapid electron transfer kinetics. By plating in situ with a bismuth film, the developed electrode exhibited well-defined and unique peaks for Zn(II), Cd(II), and Pb(II) by square wave anodic stripping voltammetry. The analytical characteristics of the BiF/N/IL/G/SPCE were explored with calibration curves, which were found to have a wide linear range of concentrations. The sensor was found to have detection limits of Zn(II) 1.38 nM, Cd(II) 0.53 nM, and Pb(II) 0.39 nM, respectively. With satisfactory results, the proposed analytical procedure was used to detect trace metal ions in drinking water samples, pointing out the suitability of the BiF/N/IL/G/SPCE to detect heavy metals in water samples. Pérez-Ràfols et al. [68] investigate the use of various carbon nanomaterial-modified screen-printed electrodes such as multi-walled carbon nanotubes (MWCNT), graphene (GPH), and carbon nanofibers (CNF) for plating Sb film and compares them to the unmodified screen-printed carbon electrode. For Lead; Pb(II) and Cadmium; Cd(II) determination, the in-situ antimony film electrode prepared from carbon nanofibers modified screen-printed carbon electrode (CNF/SPCE) exhibited superior analytical performance, according to the study. The research indicates that this electrode may be suitable for measuring low nM levels of the metals under consideration. The in-situ Sb/CNF/SPCE was utilized successfully for the simultaneous determination of Pb(II) and Cd(II) ions in a certified reference estuarine water sample, exhibiting high reproducibility and excellent accuracy. The study highlights the potential of electroanalytical devices based on screen-printed electrodes for low-cost, portable environmental quality sensors. Yin et al. [83] described the fabrication of a new type of highly active and stable Bi-based electrode material for electrochemical sensing, which consisted of BiCu metal-organic frames (MOF) derived carbon film (CF) encapsulating BiCu alloy nanoparticles (BiCu-ANPs). The incorporation of Bi and Cu to form BiCu-ANPs can enhance the electrocatalytic activity of the materials. Moreover, the carbon film that encapsulates BiCu-ANPs provides high electrical conductivity and fast electrochemical kinetics, which occur during the

adsorption and desorption of heavy metal ions. BiCu-ANPs encapsulated in carbon film (CF) (BiCu-ANPs@CF) exhibit fully exposed active sites, facile charge transfer, high stability, and conductivity, resulting in improved sensitivity and stability for electrochemical detection of heavy metal ions. When integrated to be a potable electrochemical sensing system for simultaneous detection of Lead; Pb(II), Cadmium Cd(II), and zinc Zn(II), the BiCu-ANPs@CF is modified on screen-printed carbon electrode (SPCE) It exhibits low detection limit, wide detection range, and good anti-interference. The system has been used to detect multiplexed heavy metal ions in human biological liquids (blood and urine) and environmental water, demonstrating its prospective application for on-site measurement of human health and water pollutants. Tu et al. [75] investigated and developed a miniaturized portable electrochemical system for the determination of chromium; Cr(VI) based on a screen-printed carbon electrode with gold nanoparticle modification (AuNPs/SPCE). The system sensor demonstrated high sensitivity, repeatability, and selectivity for the detection of chromium; Cr(VI) in water samples. Using the proposed sensor, real water samples were analyzed by linear sweep voltammetry (LSV), and the results were comparable to those obtained using atomic absorption spectroscopy (AAS). From its discovery, this sensor has a wide range of concentrations between 384.6 and 3846 nM and a limit of detection of 103.8 nM. Thus, the developed system sensor provides a promising platform for in-situ, rapid, and sensitive detection of chromium; Cr(VI) in environmental water. Chen et al. [87] developed a novel screen-printed carbon electrode (SPCE) modified with a three-dimensional melamine-doped graphene oxide/MXene composite aerogel (3D MGMA) for the simultaneous and sensitive detection of three metal ions (Zn(II), Cd(II), and Pb(II)) in the environment. The 3D MGMA modification provides a high surface area and functional collections, which are advantageous for enhancing electrical conductivity and promoting the absorption of heavy metal ions. The developed innovative sensing platform can detect Zn(II), Cd(II), and Pb(II) simultaneously with detection limits of 7.34 nM, 3.99 nM, and Pb(II) 1.39 nM, respectively. This sensor exhibits the viability and precision of this electrochemical sensor for detecting Zn(II), Cd(II), and Pb(II) in food (cereal) and water samples (tap water). This study proposes a creative way for monitoring heavy metal ions in the natural environment. And the last work is the modified screen-printed carbon electrode with a butterfly-shaped nanoparticle. Naseri et al. [88] proposed a simple and sensitive electrochemical sensor for the simultaneous detection of four heavy metals in water samples, including Cd(II), Cu(II), Pb(II), and Hg(II). The sensor was modified by incorporating silver nanostructures in the shape of butterflies (AgNPs), which exhibited high electrical conductivity and electrocatalytic activity. The sensor (AgNPs/SPCE) exhibited excellent stability and sensitivity for quantifying heavy metals with low detection limits. The developed sensor can be used for the electrochemical detection of water samples with high sensitivity and reproducibility. Overall, the study provides an interesting technique for on-site water analysis that can facilitate water safety evaluations.

2. Screen-printed graphene electrode

Screen-printed graphene electrodes (SPGE) have emerged as a promising alternative to conventional electrodes for the detection of metal ions in environmental and human samples. They were fabricated using a cost-effective screen-printing technique, which involves the deposition of graphene ink onto a substrate using a screen mesh. The resulting electrodes have a high surface area, good electrical conductivity, and excellent stability, making them suitable for use in electrochemical analysis.

One of the significant advantages of SPGEs is their ability to detect metal ions in real samples using various electrochemical techniques, such as SWASV, amperometry, and DPASV. This technique allows for the rapid and accurate analysis of metal ions, which is crucial for monitoring environmental and human health.

This part screen–printed graphene electrode aims to review the current research on SPGE and their application in electrochemical analysis. The focus will be on the advantages of SPGE over conventional electrodes, their sensitivity and selectivity towards metal ions, and their potential applications in the field of environmental and human health monitoring.

Table 3 The conclusion of portable electrochemical sensors in part of screen-printed graphene electrode for analysis of heavy metal ions.

Electrode	Modifier	Metal ion	Linearity (nM)	Technique	LOD (nM)	Sample	Ref.
SPGE	Graphene/ionic liquid composite	Cd(II) Pb(II)	Cd(II) 8.90 - 712 Pb(II) 4.83 - 386	SWASV	Cd(II) 0.71 Pb(II) 0.48	rice	[89]
SPGE	Polyvinylbutyral (PVB)	Cr(VI)	$3x10^3$- $1x10^7$	amperometry	$1x10^3$	acid	[90]
SPGE	2-benzothiazole-2-thiol organofunctionalized SBA-15 silica	Zn(II) Pb(II) Cu(II) Hg(II)	Zn(II) 15 - 152.59 Pb(II) 2 - 9.65 Cu(II) 6.3 - 31.47 Hg(II) 2 - 10	DPASV	Zn(II) 4.58 Pb(II) 0.314 Cu(II) 0.47 Hg(II) 0.23	ethanol fuel	[91]
SPGE	Tin nanoparticles (SnNPs)	Cd(II) Zn(II)	Cd(II) 8.90 - 267.10 Zn(II) 15.29 - 458.70	SWASV	Cd(II) 4.45 Zn(II) 4.58	tap and bottled water	[92]
SPGE	As(III) reduced with thiosulfate in an acid medium	As(III)	1.33 - 66.68	DPAV	0.79	urine	[93]
SPGE	Bismuth	Cd(II) Pb(II)	Cd(II) 44.5 - 1780 Pb(II) 48.3 - 996	SWASV	Cd(II) 2.67 Pb(II) 2.41	clinical, environmental, and food samples	[94]

SPGE = screen-printed graphene electrode, SBA = Santa Barbara Amorphous, DPASV = differential pulse anodic striping voltammetry, DPAV = differential pulse anodic voltammetry

From Table 3, we aim to discuss the works that have drawn attention for their inventiveness or their ability to detect multiple types of heavy metal using electrochemical techniques on a screen-printed graphene electrode (SPGE). Wang et al. [89] reported on the preparation of a disposable graphene/ionic liquid composite modified screen-printed graphene electrode and in-situ deposit of a Bi film on the surface of the electrode after it was modified by graphene/ionic liquid for the sensitive determination of trace lead and cadmium ions by SWASV. The obtained sensor possessed many attractive properties, such as a large surface area, good ionic and electronic conductivity, a wide electrochemical window, and high stability and sensitivity. The linear range of the electrode was for cadmium (Cd(II)) 8.90 – 712 nM and lead (Pb(II)) 4.83 – 386 nM with a detection limit of 0.71 nM for Cd(II) and 0.48 nM for Pb(II). The proposed analytical procedure was successfully used to detect trace metal ions in rice samples. The novelty of this work lies in the preparation of a highly sensitive and stable electrode for the detection of trace metal ions in complex matrices. Maria et al. [92] described the use of screen-printed graphene electrodes (SPGE) modified with tin nanoparticles (SnNP) for measuring trace levels of cadmium; Cd(II) and zinc; Zn(II). The modification sensor can analyze heavy metal ions by SWASV process. This developed sensor is fast, simple, and cost-effective, and the resulting sensors show high sensitivity and selectivity toward the target analytes. The addition of bromide ions enables well-resolved stripping peaks for cadmium, while copper interference is effectively alleviated by the addition of ferrocyanide and gallium ions. The modified electrode (SnNP/SPGE) was appropriately put to use for measuring the concentrations of Cd(II) and Zn(II) in samples of tap and bottled water. The results were satisfactory with detection limits of 4.45 nM for Cd(II) and 4.58 nM for Zn(II). The results demonstrate that the developed SnNP/GSPEs are an interesting kind of sensor for the determination of Cd(II) and Zn(II) at nanomol per liter concentrations, outweighing those previously reported in the scientific literature in terms of simplicity, cost, time, labor effort, waste loadings of the modification procedure, and low cost of the final sensor.

Ada et al. [94] have introduced a new and pragmatic method for identifying heavy metals, particularly Pb(II) and Cd(II) in diverse matrices like clinical, environmental, and food samples. The screen-printed graphene electrode was modified with Bi(III) films on its surface area via an electrochemical deposition technique. By employing a flexible, modified screen-printed graphene electrode in combination with a waxed filter paper disk for the preconcentration step of heavy metal ions, the electrochemical sensor's precision and sensitivity have been considerably enhanced, as shown in Figure 4. A straightforward preconcentration technique on the paper disk has lowered the detection thresholds for Pb(II) and Cd(II) to 2.67 and 2.41 nM, respectively, from their previous values of 17.8 and 6.28 nM. These findings reveal the potential of this inexpensive and portable electroanalytical tool for on-site measurements, which can help decrease the time and expenses associated with conventional reference techniques. And for the last work, the researcher wants to analyze two heavy metal ions using a disposable electrode because it is very easy to use and eliminate, or destroy, this sensor, and it has a few effects on the environment. Saciloto et al. [91] presented the development of an organofunctionalized modified graphite-polyurethane composite disposable

screen-printed graphene electrode for the simultaneous determination of zinc; Zn(II), lead; Pb(II), copper; Cu(II), and mercury; Hg(II) in ethanol fuel by differential pulse anodic stripping voltammetry (DPASV) techniques. This modified electrode used an ink modified with 2-benzothiazole-2-thiol organofunctionalized SBA-15 silica for a printed working electrode. The sensitivity of the modified electrode is higher than that of the bare electrode. The use of this sensor can provide a wide range of concentrations with a low limit of detection that is sufficient for the analysis of simultaneous metal ions in a real sample. Therefore, this newly developed sensor provides a very simple, low-cost, and environmentally friendly alternative to traditional methods of analysis.

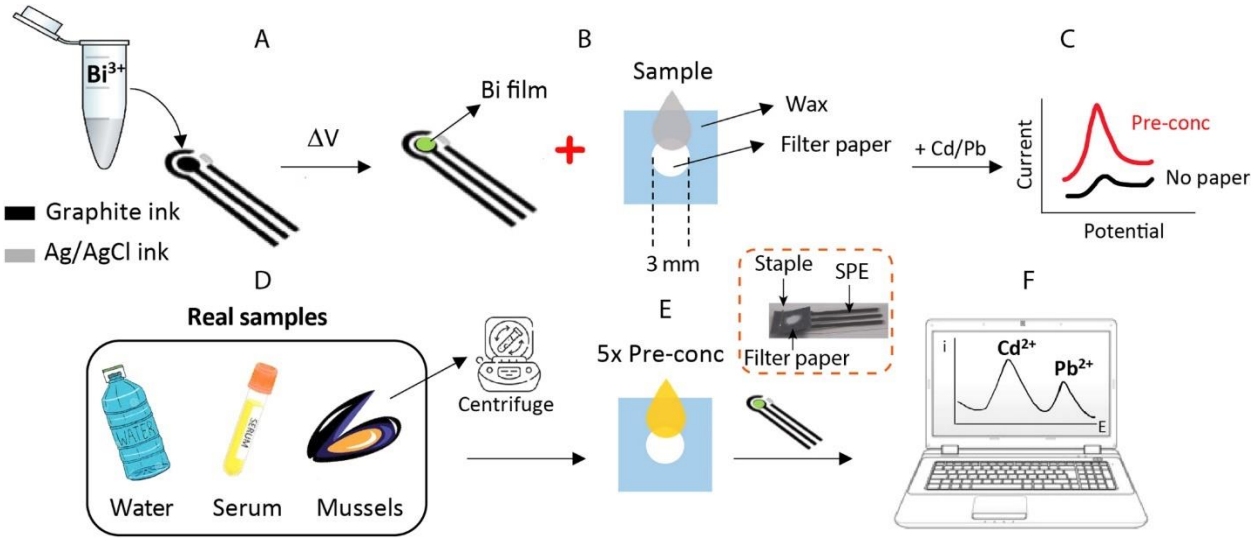

Figure 4 Schematic representation for the development of the hybrid polyester-paper platform to detect cadmium and lead in three different matrices: drinking water, human serum, and mussels. Highlight of the pre-concentration effect on the sensitivity of heavy metals detection. Reprint from Ref. [94] Raucci A, Miglione A, Spinelli M, Amoresano A, Cinti S. A hybrid screen-printed strip for enhanced electroanalysis towards lead and cadmium in multi-matrices. J Electrochem Soc. 2022;169(3):037516.

In summary, electrochemical analysis is a promising technique for detecting heavy metal ions in various samples, including environmental water, rice, ethanol fuel, tap and bottled water, urine, clinical samples, and food samples. Screen-printed graphene electrodes have demonstrated their potential as a flexible platform for modifying with different materials like graphene/ionic liquid composite, SnNPs, As(III) reduced with thiosulfate, bismuth films, etc. to improve their sensitivity and selectivity towards target analytes. This modification has led to the development of highly sensitive and selective sensors for detecting heavy metals

in different matrices. The modified sensors have exhibited excellent performance with low detection limits, a wide linear range, and remarkable stability. Screen-printed graphene electrodes modified with a range of materials hold enormous potential for use in environmental and food analysis for the detection of heavy metal ions.

3. Screen-printed gold electrode

The screen-printed gold electrode (SPAuE) has been demonstrated as a potential candidate for the detection of heavy metal ions. The SPAuE is a disposable electrode that can be easily modified with different materials to improve performance. Various modifications, such as bismuth film, amino-functionalized graphene oxide (NH_2-GO), porous graphene oxide-polypyrrole (pGO/PPy) polymer nanocomposite, self-assembled monolayers of 4-mercaptobenzoic acid, and ruthenium complex-nanoparticles-Nafion (Ru-Au/NA), have been used to enhance the sensitivity and selectivity of SPAuE for heavy metal ion detection. The modified SPAuE has been shown to have high sensitivity, low detection limits, and good stability for the detection of heavy metals such as zinc, cadmium, lead, mercury, copper, arsenic, and iron in various samples. In this part, we summarized recent advances in the modification of SPAuE for detecting heavy metal ions, focusing on the materials used and the samples analyzed.

Simultaneous analysis of Pb(II), Cu(II), and Hg(II) using a bare screen-printed gold electrode was also performed by Eduardo SA et al. [95]. They pointed to the potential application of SPAuE for the determination of trace concentrations of Pb(II), Cu(II), Hg(II) in bioethanol by SWASV techniques. The proposed method sensor had a low detection limit of Pb(II) 5.79 nM, Cu(II) 15.73 nM, and Hg(II) 8.48 nM, a wide linear concentration range of Pb(II) 24.12 – 1,446 nM, Cu(II) 78.66 – 4722 nM, and Hg(II) 29.94 – 1,496 nM, and sufficient values for the analysis of three heavy metal ions in a real sample of bioethanol. This method of analysis shows tremendous potential for on-site determination of three heavy metals in bioethanol fuel once sample preparation and electrode modifications are not required. For this work, they conclude that the proposed methods have the potential to be used for the determination of heavy metal species in fuel bioethanol and can be applied in the on-site analysis. The research provides a new method for the modification of electrode surfaces that can enhance the detection capabilities of the electrodes and improve their analytical performance, resulting in excellent quantitative analysis. And the last work is about modified SPAuE. Gold is used as a working electrode because gold is a frequent choice for the working electrode material in screen-printed electrodes in the field of heavy metal analysis integrating electrochemical sensors. Because gold is higher electrical conductivity and chemical stability, it can detect heavy metals in environmental and industrial samples with high accuracy and reliability. Furthermore, its low background noise and biocompatibility make it excellent for use in biosensing applications such as heavy metal detection in biological fluids. Albalawi I., et al. [96] proposed a novel and practical approach for determining Cd(II) and Pb(II) simultaneously in an ambient water sample utilizing a SPAuE. Graphene oxide (GO) or citrate-capped gold nanoparticles (AuNPs) and cation-exchanging Nafion polymer are used

to immobilize active ruthenium(II) bipyridine complexes on the electrode surface as shown in Figure 5. They used electrochemical techniques to examine the electrochemical behavior of hybrid Ru-GO/Nafion and Ru-Au/Nafion nanocomposites. The results showed that the Ru-GO/Nafion sensor was more sensitive to Cd(II), with a detection limit of 37.4 nM than the Ru-Au/Nafion assay, which has a poor sensitivity with a detection limit of 106.8 nM. The devised assays exhibit outstanding electrochemical performance against Pb(II), with detection limits of 25.6 nM for Ru-GO/Nafion and 12.04 nM for Ru-Au/Nafion, respectively. The hybrid nanocomposite assays were validated using atomic absorption spectroscopy (AAS) in river and tap water samples. The results of this study show that the developed approach can detect heavy metal ions in environmental water samples using a sensitive and selective analytical technique.

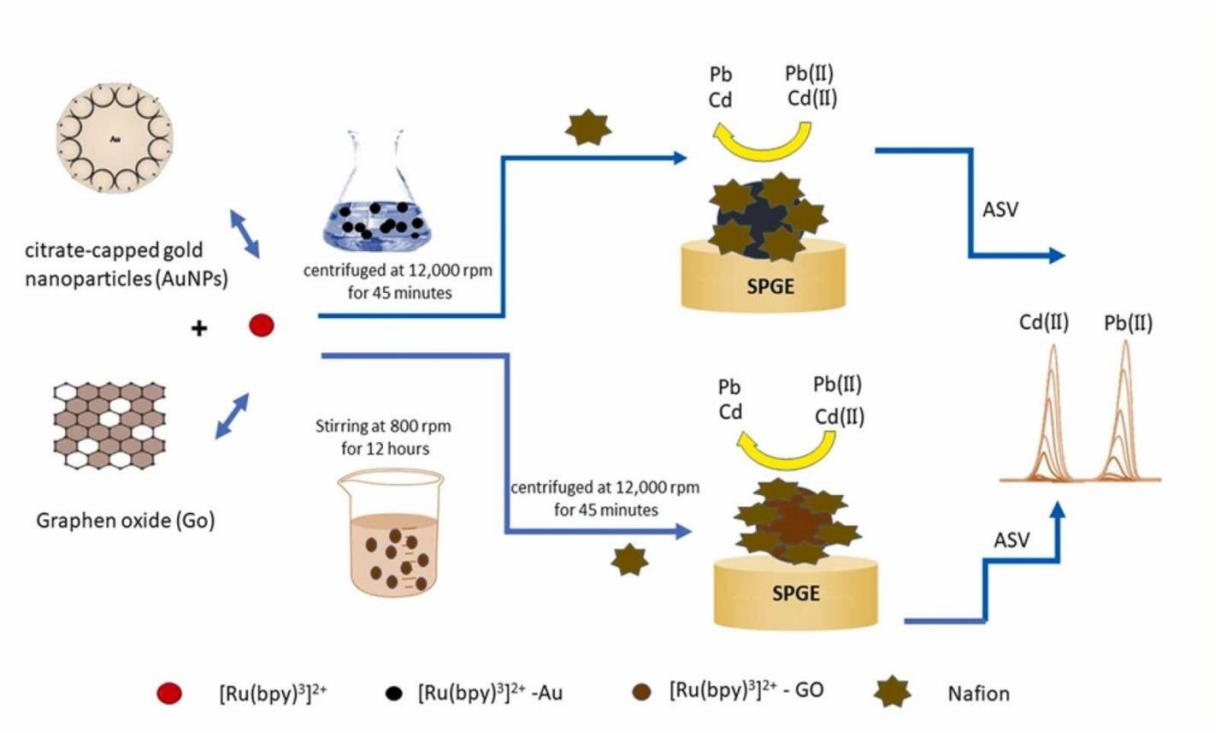

Figure 5 Schematic illustration of ruthenium (II) bipyridine complex on screen printed gold electrode surface for simultaneous determination of Cd(II) and Pb(II) in an environmental water sample. Reprint from Ref. [96] Albalawi I, Hogan A, Alatawi H, Alsefri S, Moore E. A novel comparative study for simultaneous determination of Cd(II) and Pb(II) based on ruthenium complex-nanoparticles-nafion modified screen-printed gold electrode. Sens Actuators B: Chem. 2023;380:133273.

In conclusion, the electrochemical analysis of heavy metal ions in environmental samples using screen-printed gold electrodes has been extensively studied over the years. These electrodes offer several advantages over other electrode materials, including excellent conductivity, chemical inertness, stability, and

biocompatibility. As such, they have become a popular choice for heavy metal ion analysis in various environmental and biomedical research applications.

The electrochemical detection of heavy metal ions using screen-printed gold electrodes has proven to be a highly sensitive and selective method for analyzing complex environmental samples. Researchers have demonstrated that this method can be used to detect heavy metal ions at low concentrations, making it an effective tool for environmental monitoring and pollution control. Moving forward, the use of screen-printed gold electrodes in the field of heavy metal ion analysis will likely continue to grow in popularity. With ongoing research in this area, it is anticipated that these electrodes will be increasingly used to develop new and innovative sensing technologies for the detection of heavy metal ions in environmental samples.

However, it is important to note that there are still some challenges to be addressed in using screen-printed gold electrodes for heavy metal ion analysis. For example, these electrodes may be susceptible to interference from other metal ions or organic compounds present in environmental samples, which can affect the accuracy and reliability of measurements. Additionally, the cost of manufacturing screen-printed gold electrodes can be a limiting factor for widespread adoption in certain research settings. Despite these challenges, the use of screen-printed gold electrodes in heavy metal ion analysis remains a promising area of research with significant potential for improving our understanding of the impact of heavy metal pollution on the environment and human health. With continued innovation and research in this field, these electrodes will likely become an increasingly important tool for environmental monitoring and analysis in the future.

Table 4 The conclusion of portable electrochemical sensors in part of screen-printed gold electrode for analysis of heavy metal ions.

Electrode	Modifier	Metal ion	Linearity (nM)	Technique	LOD (nM)	Sample	Ref.
SPAuE	Bare	Pb(II) Cu(II) Hg(II)	Pb(II) 24.12 - 1446 Cu(II) 78.66 - 4722 Hg(II) 29.94 - 1496	SWASV	Pb(II) 5.79 Cu(II) 15.73 Hg(II) 8.48	fuel bioethanol	[95]
Gold microelectrode	Amino-functionalized graphene oxide (NH_2-GO)	As(III)	13.35 - 144.50	SWASV	2.16	ground water	[97]
SPAuE	Bare	Cu(II)	15.7 - $1.1x10^{-4}$	SWASV	23.6	biodiesel	[98]
SPAuE	porous graphene oxide-polypyrrole (pGO/PPy) polymer nanocomposite	Cd(II)	8.90 - 890	DPASV	0.44	tap, pond and river water	[99]
SPAuE	Bare	Pb(II) Cu(II) Hg(II)	Pb(II) 24.1 - 217 Cu(II) 78.6 - 709 Hg(II) 24.9 - 224	SWASV	Pb(II) 6.27 Cu(II) 3.14 Hg(II) 4.49	struvite	[100]
SPAuE	self-assembled monolayers of 4-mercaptobenzoic acid	Hg(II)	0.03 - 245	ASV	0.005	fish muscle	[101]
SPAuE	ruthenium complex gold-nanoparticles-nafion (Ru-Au/NA)	Cd(II) Pb(II)	Cd(II) 890 - 2670 Pb(II) 48.2 - 1450	SWASV	Cd(II) 106.8 Pb(II) 12.04	environment water	[96]

SPAuE = screen-printed gold electrode, SWASV = square wave anodic stripping voltammetry, DPASV = differential pulse anodic stripping voltammetry, ASV = anodic stripping voltametry

Conclusions

The research under review suggests that the measurement of metal ions is an essential component of food, clinical, environmental, and industrial monitoring. Not only are metal ions recognized to be harming human health and the environment, but they also need to be quantified for quality control. As a result, there is an increasing need for effective and trustworthy analytical methods for locating and measuring metal ions in real-world samples. Traditional electrochemical sensors are several advantageous for analyzing metal ions in samples. However, they frequently call for pricey electrode materials that are only useful in a lab, and require reagents and chemicals. Therefore, to enable simple, affordable, rapid in-field metal detection devices, research must concentrate on the development of portable/cost-effective metal detection technologies. Screen-printed technology provides a straightforward, adaptable, low-cost, and highly sensitive method that has the potential to be the foundation of a new generation of portable electrochemical sensors for trace-level ion in-situ metal sensors. The combination of inexpensive, calibrate-free, and customizable screen-printed electrodes with electrochemical techniques made available by miniature and portable potentiostats is a promising candidate to enable this evolution. These stepwise changes bring about the creation of metal-ion electrochemical sensors that can fulfill the newly specific requirements and can be applied for real-time analysis.

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