Review

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Novel Aspects in the Voltametric Determination of Heavy Metals: A Minireview

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Abstract: Heavy metals represent a class of chemical elements that includes metalloids, bases and transition metals, lanthanides and actinides. They are distinguished for their toxicity in small concentrations and for their negative effects on the environment and human health. They are present in various samples, mainly in water, industrial waste and food. The determination of heavy metals is carried out mainly by analytical methods, using spectroscopy, spectrometry and electroanalysis, while studies are being carried out for the development of new and faster methodologies and techniques for their analysis, with particular emphasis on voltammetry. This review deals with the determination of heavy metals mainly in environmental samples (water) using voltammetry. In particular, the methods of their determination are evaluated in terms of sensitivity, selectivity and applicability.

Keywords: heavy metals; voltammetry; environmental applications; differential pulse voltammetry (DPV); square wave voltammetry (SWV); water analysis

1. Introduction

The characterization of pollutants that contaminate our environment is very important in the assessment of human exposure and of ecosystem risk. Due to the extremely high number of chemicals found in the environment, the sampling and the chemical analysis of contaminated environmental samples can be time consuming and expensive, thus limiting the number of samples that can be analysed.

During the last years, there have been increasing issues addressing the possible impact industrial activities on the environment. Consequently, the ability to monitor contaminants in the environment has crucially improved managing risks to human health and ecosystems. Regarding the environment, discharges related to the industrial activities represent a potential threat to the ecosystem since they contain xenobiotics like heavy metals. Heavy metals are associated with different toxic effects that may cause immediate or long-term damage to the environment and may constitute a hazard to public health, prolonged exposure to elevated levels of these metals is linked to various health issues. Besides this, heavy metal accumulation may result to ecosystem imbalances and biodiversity loss As a consequence many countries have established water quality standards that include concentration limits for heavy metals. Monitoring and detecting these metals in water is crucial to ensuring compliance with regulatory guidelines and protecting public health. The detection of heavy metals helps identify and trace the sources of contamination, whether they are from industrial discharges, agricultural runoff, or other anthropogenic activities. This information is essential for implementing targeted pollution control measures. Regarding the importance of environmental analysis mainly water analysis is very crucial as it represents a critical tool for safeguarding human health, protecting the environment, ensuring regulatory compliance, and supporting sustainable water management practices. Moreover, for assessing the potential risk for human exposure, ecosystem, water resources etc. is nowadays requested to integrate the physicochemical information within ecotoxicology and biomonitoring.There is a requirement of use of analytical methodologies that are pertinent, applicable in the field, quick and yet cost-effective allowing sample preparation simplicity, real time monitoring and equipment accessibility [1–9]

Thus most cost effective, rapid, field screening and monitoring methods are more and more requested in order to increase of information concerning the location, source and concentration of pollutants which may impact human health and the environment.

Voltammetry is preferred for the detection of heavy metals possessing the advantages of low cost, simplicity, ease of operation, fast analysis, portability, the ability to monitor environmental samples in the field, and high sensitivityand selectivity.

In the present review, are being critically summarized, the applications of voltammetry in the determination of heavy metals in environmental and mainly in water samples.

1.1. Determination of Pb

The determination of lead in water samples has been studied by anodic voltammetry (ASV), using a copper-shaped carbon electrode (Cu-CE). The electrolyte used was a buffer solution of 0.01 M HCl and 1 M KCl. The selective determination of Pb was successful by adjusting the electrodeposition potential and showed a low LOD, 1 μM [10]. A glassy carbon electrode formulated with eDAQ has also been used in a solution of 1 M KNO_3 electrolyte. The technique yielded satisfactory results in the selective determination of Pb as the only significant inhibition was caused by Se. The proposed technique has a high probability of replacing conventional reagent-based sample preparation methods for detection of Pb in tap water [11].

With square wave voltammetry (SWV), Pb has been detected in tap water, well and thermal water by forming a carbon paste electrode with geopolymer cement (CPE/GP-Dib_2). A 0.2 M $NaNO_3$ solution was used as an electrolyte and the results showed that the sensor offered high selectivity for Pb^{2+}, with an LOD equal to 2.3×10^{-9} M [12]. Square wave voltammetry has been combined with anodic stripping voltammetry (SWASV) to detect Pb^{2+} ions. A study conducted with SWASV used an electrode printed with an ink injection printer, molded with multiwall carbon nanotubes (IJP-MW-CNT electrode), electrolyte with a 0.1 M acetate buffer. The LOD of the IJP-MW-CNT sensor in drinking water was calculated to be below the maximum contamination level for the World Health Organization (WHO) and the Environmental Protection Agency (EPA) (LOD 1.0 μg/L, LOQ 3.5 μg/L). The LOD was calculated on a drinking water sample without the need for in-situ membrane formation, electrolyte or pH adjustment [13]. Another technique involves detecting Pb with a lithographically printed electrode, shaped with Bi and hierarchically tubular and porous biochar (Bi/PTBC800/SPE). With 0.1 M acetate buffer and pH 4.5, and under optimal conditions, PTBC gave much better analytical performance for detecting Pb^{2+} ions (LOD 0.02 μg/L), compared to previous similar techniques [14]. The lithographically printed carbon electrode molded with dopamine polymer and polypyrolle hydrogel (PDA-PPy/SPCE) provided satisfactory results with an LOD equal to 0.15 μg/L and signal amplification was carried out with improved conductivity and catalytic capacity [15]. SWASV detected Pb in food samples with an Fe_3O_4-shaped glassy carbon electrode in a Schiff base network (Fe_3O_4@SNW1/GCE). As an electrolyte a solution of 1.0×10^{-1} mol L^{-1} KNO_3 was used. The proposed electrode showed a linear response to Pb in the concentration range of 0,003-0,3 μmol/L with a LOD of 0,95 nmol/L. The results obtained showed that this method exhibited appropriate selectivity, stability, repeatability and reproducibility [16]. Using the same voltammetric technique, tap water samples were studied with an electrolyte 0.1 M acetate buffer, pH 4.5. A graphene oxide electrode was used, which was formed with N and Bi. The GO Bi and N electrode showed remarkable electrocatalytic activity for the detection of Pb^{2+} compared to the individual Bi- and N-doped GO electrodes as measured by cyclic voltammetry (CV). The formation of electroactive double positions Bi and N significantly enhances the adsorption of Pb^{2+} ions as well as the deposition-redissolution process, while their synergistic interaction in electron transfer and catalysis is responsible for the significantly sensitive detection (LOD 10.9 pM, LOQ 36.4 pM) [17]. Pb ions were found in water and soil samples near a plant with a glassy carbon electrode molded with Bi- and Bi_2O_3 (Bi/ Bi_2O_3@C/GCE) and 0.1 M acetate buffer as an electrolyte. This material, which preserved the structure of Bi-MOFs, had a relatively large specific surface, as well as high electron transfer capabilities. It had a wider linear range, a detection limit equal to 6.3 nM, good stability, reproducibility, selectivity and comparable performance to the ICP-MS method in different samples [18]. Another study used a glassy carbon electrode molded with two-dimensional blue MXene (CoPB-MXene/GCE) in 0.01 M phosphate buffer at pH 6.5. The electrode showed high selectivity despite the introduction of different blocking ions in the detection process of Pb^{2+} [19].

A recent paper used linear– sweep voltammetry (LSV) in combination with anodic stripping voltammetry (LSASV). This research involved forming a carbon paste electrode with clay, and detecting Pb ions in water and biological samples, using the 0.1 M KCl solution as an electrolyte. The mechanism of filtration of Pb on the surface of a ceramic microfiltration membrane, made of a mineral clay lamp, was studied. The Pb ion accumulated well on the clay membrane/electrode surface at a low pH, 1.5. At higher pH (pH > 7), Pb precipitated as $Pb(OH)_2$ which resulted in zero accumulation of Pb on the surface of the clay membrane of the electrode [20].

Pb has also been determined by differential pulse anodic stripping voltammetry (DPASV) in three different commercial products used as progressive hair dyes. The technique involved a cork-graphite composite sensor and two different electrolytes. The 0.5 M H_2SO_4 solution gave better results for the sensitivity of the substance to be analysed compared to acetate buffer. For 0.5 M H_2SO_4 solution the LOD and LOQ limits were 4.36 μM and 1.06 μM, respectively, while for 0.1 M acetate buffer pH 4.5 was 3.29 μM and 1.26 μM, respectively. The standard DPSV addition method was successfully applied to quantify Pb in hair dye samples, yielding values below 0.45% in Pb [21]. In analysis of tap water and groundwater samples, Pb was detected by differential pulse anodic voltammetry using a polypyrrole-molded glassy carbon electrode, Bi film and metal organic framework (MOF) (BF-PPy/UIO-66-NH_2/GCE) and 0.5 mmol/L $K_3[Fe(CN)_6]$ and 1 mol/L KCl as electrolyte. The electrode gave a wide linear range (0.5 to 10 μg/L) with a low limit of detection (0.05 μg/L). It also showed remarkable resistance to blocking ions, repeatability and stability [22]. Another technique used a bismuth film, Nafion and a nitrogen-admixed worm carbon frame that formed a glassy carbon electrode (Nafion-WNCF/BFGCE). Under optimal experimental conditions, the formatted glassy electrode (Nafion-WNCF/BFGCE) exhibited a wide linear range from 0.5 mg/L to 100 mg/L and a low detection limit of 0.2 mg/L. All results showed that WNCF can be considered as a green and low-cost nanomaterial [23].

1.1.1. Simultaneous Determination of Pb and Cd

The simultaneous determination of the ions of the heavy metals lead and cadmium in a variety of samples, mainly water, is the most widespread, based on the literature. Square wave voltammetry (SWV) and differential pulse voltammetry (DPV) were also very helpful in this case as they gave remarkable results, with low detection limits that are in line with the limits established by individual health assurance bodies.

One of the techniques for detecting these metals in coastal and transitional waters, by anodic stripping voltammetry (ASV), involved the use of Hg film electrode (MFE). The LODs for Pb and Cd ions were calculated equal to 4.0 ng/L and 0.50 ng/L respectively [24]. In natural brine samples, Pb and Cd were determined using a hanging Hg drop electrode (HMDE). The proposed procedure allowed the determination of Cd (0.001 μg/L) and Pb (0.005 μg/L) after only 100 times dilution as samples, such as brine, with so high salinity must be significantly diluted. LOQs were found below recommendations related to brine use in balneotherapy [25]. In another method, a copper film electrode (Cu-FE) was used, having as electrolyte the solution of 0.1 M HCl and 0.4 M NaCl. The low limits of detection (LOD 0.6 μg/L, 1.8 μg/L and LOQ 1.7 μg/L, 5.6 μg/L for Pb and Cd respectively) showed that Cu-based electrodes are a promising solution for Hg electrode replacement and for an environmentally friendly anodic voltammetry [26].

Square wave voltammetry (SWV) simultaneously detected Pb and Cd ions in water samples with a carbon paste electrode formed with Bi film (BiFE-CPE). The auxiliary electrolyte was a 0.01 M acetate buffer at pH 4.6. The proposed method was accurate and sensitive.. The resulting electrode is very cheap compared to the solid electrode and not toxic at all [27].

Square wave anodic stripping voltammetry has also been widely exploited, with one of the methods involving a lithographically printed graphite-based electrode covered with Nafion. A 50 mM NaCl solution pH 4.6 served as an electrolyte. The graphite-based Nafion-coated electrodes were stored in different humidity and temperature conditions and analyzed using anodic square wave analytic voltammetry, cyclic voltammetry, electrochemical impedance spectroscopy and scanning electron microscopy. The study of the different conditions was decisive in extracting results as the morphological and conductive properties of Nafion thin films have a strong dependence on environmental conditions. Significant differences were observed in changing humidity conditions, with enhancing the electrochemical performance of sensors at lower humidity [28]. Another technique involves the use of a carbon paste electrode molded from multiwalled carbon nanotubes and antimony trioxide (Sb_2O_3/CNTCPE). As an electrolyte, a 0.01 M HCl solution was used to detect Pb and Cd ions in water samples. The comparison of the new method with GFAAS (graphite furnace atomic absorption spectroscopy) in real samples, revealed that the new SWASV method for the determination of Cd^{2+} and Pb^{2+} ions is free of systematic errors and gave low detection limits equal to 1.2 μg/L and 1.7 μg/L respectively [29]. A lithographically printed black carbon electrode has also been molded with poly(propyleneimine) (SPE-CB-PPI) creating a sensitive sensor with low limits of detection (3.6 μg/L, 15.3 μg/L) in the determination of Pb and Cd metals in water samples, amplified by the 0.1 M acetate buffer electrolyte and pH 4.6 [30]. Glassy carbon electrodes have found wide application in the detection of the desired metals giving good results in terms of sensitivity and selectivity. One of them was formulated with nanocomposite reduced graphene oxide decorated with $(BiO)_2CO_3$ and Nafion [$(BiO)_2CO_3$ -rGO-Nafion/GCE] and gave low detection limits of up to 0.24 μg/L for Pb and 0.16 μg/L for Cd, in a 3 M KCl solution [31]. Another glassy carbon electrode was formed with polythionine (in the presence of Bi) and multiwalled carbon nanotubes (Bi-PTH/MWCNTs/GCE). With a acetate buffer, 0.1 M and pH 3.5, Pb and Cd ions with LOD of 0.4 nM and 0.6 nM respectively were determined. PTH improves detection functionality. PTH is more sensitive to Pb^{2+}, so on the presence of Bi^{3+}, they can have a complementary effect [32]. To detect ions in seawater and tap water samples, a carbon glassy electrode with carbon combined with N and Ti_3C_2-MXene (Ti_3C_2@N-C/GCE) was formed. In a solution of 5 mM $[Fe(CN)_6]^{3-/4-}$ and 0.10 M KCl, ions with low detection limits of 1.10 nM (Pb) and 2.55 nM (Cd) were found. Ti_3C_2@N-C/GCE is more sensitive to Pb^{2+} than to Cd^{2+} and showed excellent selectivity for these two ions in the presence of blocking ions and molecules [33]. Another technique involved the study of deep eutectic solvents for the microextraction of liquid-liquid reverse phase dispersion of lead and cadmium in vegetable oil samples, using an Hg-shaped electrode and a 0.1 mol/L HCl solution as electrolyte. The detection limits were calculated equal to 0.01 μg/kg and 0.06 μg/kg [34]. For the detection of Pb and Cd ions with high linear range, sensitivity and stability, a nanoporous Bi glassy carbon electrode was formed, which is superficially decorated with Bi_2O_3 (Bi_2O_3@NPBi/GCE). After coating an amorphous layer of Bi_2O_3 on the surface of NPBi the results were satisfactory, with an LOD of 0.02 μg/L (Pb) and 0.03 μg/L (Cd) [35]. In samples of rice water, raw milk and tobacco extract, Pb and Cd ions with low detection limits of 0.012 ng/L and 0.02 ng/L respectively were found using a 0.1 M acetate buffer solution and an electrode formed with salicylidene-2-amino benzyl alcohol and multiwall carbon nanotubes (SABA/MWCNTs electrode). This technique showed good conductivity and fast electron transfer [36]. One method of determining the desired ions in wastewater utilized a lithographically printed electrode which was shaped with Nafion. A 0.1 M acetate buffer served as an electrolyte carrier. The proposed electrode showed greater affinity for Pb^{2+} ions due to the presence of ligand-SO_3^{2-} on the electrode surface, as it was demonstrated by the maintained peak of Pb^{2+} intensity. The low limits of detection for ions are 8.4 μg/L and 0.032 ppm for Pb and Cd [37].

Differential pulse anodic stripping voltammetry (DPASV) is one of the most applied electroanalytical techniques for the detection of heavy metals and specifically for the ions of the metals Pb and Cd. In samples, certified estuarine water samples have been combined with a lithographically printed two-dimensional carbon electrode which is shaped with bismuthene (2D Biexf-SPCE). The use of 2D Biexf-SPCE for the detection of Pb^{2+} and Cd^{2+} ions yielded low LOD limits (0.06 μg/L, 0.07 μg/L) and LOQ, high sensitivities, good repeatability and reproducibility [38].

Another recent technique involves a molded glassy carbon electrode with silane bentonite decorated with Ag nanoparticles (AgNP@Bt/TC/GCE). The electrode with the help of the supporting electrolyte (acetate buffer 0.1 M, pH 4.5) gave low detection limits 0.88 μg/L (Pb) 0.79 μg/L (Cd). Its stability was proved by repeated measurements . The presence of several interference ions did not affect the detection of the two ions, although the presence of Zn^{2+} showed well-separated oxidative peaks [39]. A glassy carbon electrode was also formulated with polyrutin and Ag nanoparticles (polyrutin/AgNPs/GC) for the simultaneous determination of Pb and Cd metals in water, soil and wool samples. With polyrutin/AgNPs/GCE, experimental parameters such as carrier electrolyte, ambient pH, deposition potential and preconcentration time were studied. The detection limits were found at low levels of 3 nM and 10 nM for the two metals respectively [40].

In natural water samples, the two metals were also detected simultaneously and individually with the LODs of the simultaneous determination being equal to 0.018 nM (Pb) and 0.023 nM (Cd). The working electrode was a pencil graphite electrode formatted with polypyrrole and CO_2 (PPy-CO_2@PGE), while 0.1 M acetate buffer was used as the carrier electrolyte. A glassy carbon electrode formatted with Sb and Bi (Sb/Bi-GCE) gave good results in terms of sensitivity and low detection limits (0.01 μg/L, 0.5 μg/L) of the metals Pb and Cd. The preparation of the Sb/Bi-GCE electrode was quite simple and less time consuming [42]. A similar technique involved a glassy carbon electrode molded with Nafion and Bi nanoplates (Nafion/BiNP/GCE), a 0.1 M acetate buffer (pH 4.5) as an electrolyte, and gave detection limits equal to 0.178 nM (Pb) and 0.376 nM (Cd). The Nafion/BiNP/GCE electrochemical sensors successfully detected Cd^{2+} and Pb^{2+} in tap water and wastewater, despite the presence of inhibitors in both samples [43]. A lithographically printed two-dimensional microfiber electrode formatted with Sb (2D Sbexf-SPCNFE) was used in the successful simultaneous detection of metals and gave satisfactory limits of detection (LOD: 0.1 μg/L for Pb and 0.9 μg/L for Cd) and quantification (LOQ 0.3 μg/L for Pb and 2.9 μg/L for Cd), good reproducibility and fidelity. A solution of HCl 0.01 mol/L and pH 2 was used as the ~~s~~supporting~~-~~electrolyte. The excellent analytical effect of the electrode is due to the synergistic effect of the properties of both fused nanomaterials [44]. Another technique involved a rotating disc glassy carbon electrode which was also formed with Sb (Sb-GC-RDE) and a 0.01 M HCl solution. In situ preparation of the molded electrode is an effective strategy for improving the performance of the commonly used GC electrode. Thus, the technique gave low detection limits equal to 1.1 μg/L, 1.4 μg/L for the metals Pb and Cd in soil and soil water samples [45].

In rice, honey and vegetable samples, the ions of the metals Pb and Cd were detected simultaneously and successfully by forming a glassy carbon electrode, molded with carbon black and polyriboflavin in the presence of Bi (Bi-PRF/CB/GCE). RF electropolymerization performed on the surface of CB/GCE played a complementary role with Bi^{3+} for the selective determination of Pb^{2+} and Cd^{2+}. Specifically, PRF is more sensitive to Pb^{2+} while Bi^{3+} is more sensitive to Cd^{2+}. The LOD limits were calculated to be equal to 0.13 nM and 0.16 nM for Pb and Cd respectively [46]. For the determination of these metals in samples of charcoal from coffee tree bark, differential pulse adsorptive stripping voltammetry (DPAdSV) was applied with a charcoal-molded carbon paste electrode (BC-CPE). The metals were successfully detected with an LOD of 0.2 μg/L (Pb) and 1.7 μg/L (Cd), with a solution of 0.1 M acetate and pH 4.8. Some of the advantages of this new sensor are the use of environmental pollutants (coffee husks) for electrode forming, "zero cost" and green production, as well as its very simple preparation [47]. Soil samples have been analysed with a glassy carbon electrode formed with Bi (Bi/GCE), with voltammetry SWASV, in 0.2 M acetate buffer, pH 5. The Feature-RF model reduced the RMSEV value of Cd^{2+} from 10.941 μg/L to 1.439 μg/L and the Feature-SVR model reduced the RMSEV value of Pb^{2+} from 32.199 μg/L to 5.348 μg/L [48]. In environmental waters were also simultaneously detected Pb and Cd ions using a glassy carbon electrode (GCE) coated with poly(amidoamine) dendrimer functionalized magnetic graphene oxide (GO-Fe_3O_4-PAMAM), with SWASV. This technique sawed satisfactory results, with low detection limits of 130 ng/L for Pb(II) and 70 ng/L for Cd(II), high sensitivity and good anti-interference capability [49].

1.1.2. Simultaneous Determination of Pb, Cd and Hg

Simultaneous determination of Pb, Cd and Hg has been performed in water samples, utilizing anodic voltammetry. The electrode was a 3D-printed graphene and polylactic acid electrode and as an electrolyte a 1 mM solution of FcMeOH. Hg was easily measured at trace levels with a 6.1 nM LOD in unformatted graphene/PLA, but Pb and Cd required Bi microparticles to reach the required detection limits [50]. By differential pulse stripping voltammetry metals were determined in samples of liquid foods, namely orange juice, apple juice and cow's milk. A nanoelectrode was formed with Au and the results gave low detection and quantification limits for Pb, Cd and Hg equal to 1.0 μg/L, 1.1 μg/L, 1.2 μg/L and 3.0 μg/L, 3.3 μg/L, 3.6 μg/L respectively. The mobile phone-based electrochemical platform enabled sensitive and affordable monitoring of heavy metals in popular liquid foods, with minimized requirements for laboratory instruments and technical expertise [51]. With the same electroanalytical technique, metals were detected in tap and river water samples in a 0.1 M HCl solution. A carbon paste electrode with Na_2CO_3 and active Hordeum vulgare L. (HVW-Na_2CO_3/CPE) powder was made as the working electrode. This technique showed high sensitivity and high selectivity providing LOD limits equal to 0.0691 nM, 1.82 nM and 0.237 nM for the metals Pb, Cd and Hg [52].

1.1.3. Simultaneous Determination of Pb and Cu

In wine samples, ions of the metals Pb and Cu were found simultaneously by anodic stripping voltammetry. A glassy carbon electrode was formed with Nafion and $MnCo_2O_4$ (Nafion/ $MnCo_2O_4$/GCE) and in HCl/KCl buffer (0.1 mol/dm^3) the metals Pb and Cu were detected with low limits of detection (1.67 μg/dm^3, 7.14 μg/dm^3) and quantification (5.5 μg/dm^3, 23.6 μg/dm^3). Under appropriate conditions, calibration curves were linear in the range 0.01-8 and 0.01-5 mg/dm^3 for Pb and Cu, respectively, and the effect of sample dilution, pre-concentration time and potential were optimised [53]. In another work, a hydroxyapatite (Hap/CE) shaped carbon electrode was constructed to detect Pb and Cu in water samples, with a solution of 1 M KNO_3, as the carrier electrolyte. While the sensitivity to detect copper pollution was sufficient, it was not satisfactory for lead United States Environmental Protection Agency. The 92% w/w hydroxyapatite composite, which showed a ratio of approximately 1:1 between the exposed region of hydroxyapatite and carbon (by the Brunauer-Emmett-Teller method), always showed a mean maximum redissolving oxidation intensity of approximately 250 μA/cm^2 and 150 μA/cm^2 for a 50 μM Pb^{2+} and Cu^{2+} solution, respectively [54]. For the determination of Pb and Cu ions in lake water samples, a glassy carbon electrode was formed with multiwall carbon nanotubes, Nafion and ZIF-67 (ZIF-67/MWCNT/Nafion-GCE). The analysis was performed with a square pulse stripping voltammetry and an electrolyte a 0.1 M acetate buffer at pH 2.0. This electrode gave a wide linear range, extremely low LOD (1.38 nM, 1.26 nM for Pb, Cu respectively), good sensitivity, repeatability, reproducibility, anti-interference capability, stability, specificity and applicability to real samples [55]. Another technique involves the use of a graphite electrode formulated with caffeic acid (GE/poly(CA)) in samples of artisanal sugar cane distillate, with a solution of 1 M HNO_3. The acidic medium produced an excellent polymer film that served in the simultaneous detection of metals. Excellent linear range, repeatability, reproducibility and recovery were observed, with LOD limits calculated at 3.01 μg/L and 4.50 μg/L for the two metals Pb and Cu, respectively [56].

1.1.4. Simultaneous Determination of Pb, Cd and Cu

In the analysis of the determination of the three metals Pb, Cd and Cu, a carbon paste electrode molded with a shell core of Bigarreau Burlat, one of the most widespread cherry varieties (BBKS-CPE) has been used with square wave voltammetry. A 0.2 M acetate buffer formed the carrier electrolyte and the results gave low detection limits of 8.48 μg/L, 9.56 μg/L, 9.77 μg/L and good accuracy. The electrode showed stability and selectivity in detecting these metals in seawater, tap water and industrial wastewater samples. The BBKS-CPE molded electrode can be applied as an environmentally friendly and low-cost electrochemical sensor [57]. Square-pulse stripping voltammetry simultaneously detected the cations of these metals in water samples, with a microelectrode molded with high-density carbon nanotube fiber rods (HD-CNTf). The technique, exhibited exceptional sensitivity and detection limits well below those set by the EPA and WHO, and was equal to 0.45 nM (92 ng/L) in tap water and 0.26 nM (55 ng/L) in simulated drinking water for Pb, 0.24 nM (27 ng/L) in tap water and 0.25 nM (28 ng/L) in simulated drinking water for Cd and 6.0 nM (376 ng/L) in tap water and 0.32 nM (20 ng/L) in simulated drinking water for Cu [58]. Another technique involved the use of gel-embedded antifouling microelectrode arrays (GIME) for the simultaneous detection of Pb, Cd and Cu. An innovative underwater detector (TracMetal) was used, with surface water sampling to quantify the targeted trace metals in the dissolved fractions <0.2 μm and <0,02 μm to suspended particulate matter and phytoplankton nets at the mouth of an estuary. The limits of detection were calculated equal to 1 ng/L, 0.7 ng/L and 6.6 ng/L respectively [59]. A glassy carbon electrode was formed with Fe_3O_4 and D-valine (Fe_3O_4-D-Val/GCE) for the simultaneous determination of Pb, Cd and Cu metals in water samples, with 0.1 M acetate buffer. The technique showed excellent selectivity, sensitivity and low LOD equal to 18.89 nM, 18.38 nM, 7,481 nM respectively for Pb, Cd and Cu [60]. For the same purpose, a sensitive glassy carbon electrode has also been formed and shaped by the ZnO and Nafion nanostructure (ZnO-NP-Nafion/GCE). In a solution of 0.1 M KCl and 5 mM $[Ru(NH_3)_6]_3$ were made measurements and it appeared that the working electrode is a sensitive electrode, with good electrochemical characteristics and efficient analytical parameters for the detection of heavy metals, and gave low LOD limits equal to 11.88 nM (Pb), 16.21 nM (Cd) and 47.33 nM (Cu) [61].

Differential pulse voltammetry has also found application in the simultaneous detection of metals Pb, Cd and Cu. One technique used a hanging Hg drop electrode (HDME) in combination with magnetic $Fe_3O_4@SiO_2$-cyclene nanoparticles, with a 0.5 M KCl solution at pH 6.0. Magnetic $Fe_3O_4@SiO_2$-cyclene nanoparticles were developed and used as an adsorbent for Pb, Cd and Cu but also as a means to eliminate ions of these metals from individual and mixed solutions by titrating nanocomposites on suspension. It was needed the smallest amount of nanoparticles to bind Cu^{2+} [62]. In agricultural irrigation water samples, the three metals were detected simultaneously with a boron-sensitive biocarbon electrode (B-bioC/MEDs). In a 0.1 M acetate buffer, this electrode has high conductivity and excellent electrocatalytic action for simultaneous electroanalysis of metals. The LODs calculated were quite low and equal to 4 nM, 54 nM, 24 nM for the cations of the metals Pb, Cd and Cu respectively [63].

1.1.5. Simultaneous Determination of Pb, Cd, Cu and Hg

A lithographically printed carbon electrode was molded with Ag nanoparticles (AgNS/SPCE) to simultaneously determine the metals Pb, Cd, Cu and Hg in tap water, rainwater and lake samples. Due to the excellent electrical conductivity and high electrocatalytic activity of AgNS, two distinct upward signals were recorded for Cd and Pb in AgNS/SPCE. LOD levels were below the permissible limits, 2.5 μg/L, 0.4 μg/L, 0.73 μg/L and 0.7 μg/L [64]. In milk samples, the metals Pb, Cd, Cu and Hg were also detected simultaneously by means of a glassy carbon electrode magnetite molded with Fe_3O_4 and silica ($Fe_3O_4@SiO_2$/MGCE). In a buffer solution of 0.1 M acetate and pH 5, the LODs were calculated equal to 16.5 nM, 56.1 nM, 79.4 nM and 56.7 nM respectively. The method proved economical, sensitive and simple [65].

1.1.6. Simultaneous Determination of Pb, Cd and Zn

Cations of the heavy metals lead, cadmium and zinc have been detected in fish feed by anodic voltammetry. The electrode was an electrochemical fluid injection molded granule, consisting of three conductive polymer electrodes loaded with carbon fibers embedded in a plastic liquid support, while a 0.1 M acetate buffer served as the carrier electrolyte. The experimental variables (concentration of bismuth plating solution, deposition potential, sample volume, stripping method) were investigated and possible interference was evaluated. The limits of quantification were 2.8 μg/L, 3.6 μg/L and 4.2 μg/L for the three metals respectively [66]. To determine the specific metals in water samples, a square pulse anodic voltammetry was constructed, a pencil graphite electrode molded with multiwall and Bi carbon nanotubes (MWCNT/Bi/PGE) was constructed. This technique proved easy, selective, and highly sensitive as it was combined with a low-cost effective graphite electrode. It gave satisfactory limits of quantification (0.89 μg/L, 1.44 μg/L, 5.43 μg/L for Pb, Cd and Zn) and detection (0.27 μg/L, 0.43 μg/L, 1.63 μg/L) [67]. With the same voltammetric method, these metals were simultaneously detected using a lithographically printed carbon electrode molded with poly(3,4-ethylenedioxythiophene) fibers with aqueous polyvinyl alcohol solution and Ag nanoparticles (PEDOT/PVA/AgNPs fibers-modified SPCE). AgNP can increase the conductivity of composite fibers and act as nucleation sites for Zn deposition resulting in increased sensitivity of Zn detection. In a 0.1 M acetate buffer and pH 4.6, Pb metal cations were successfully detected with low detection limits of 8 μg/L, 3 μg/L and 6 μg/L, Cd and Hg in drinking water samples [68]. Another technique studied samples of pasteurized milk, apple juice and drinking water with a carbon paste electrode molded with CuO and $TbFeO_3$ ($TbFeO_3$/CuO/CPE) in acetate buffer with pH 4.8. The electrode has high detection capabilities for lead, cadmium and zinc in water and food samples giving low detection limits of 0.12 mg/L, 0.29 mg/L and 0.48 mg/L respectively. In addition, it is affordable and environmentally friendly [69]. In a recent study to detect metals in water samples, a carbon paste electrode was formed with Bi and Sb (Bi-Sb/CPE). In acetate buffer with pH 5.6, the limits of detection were calculated fairly low with values of 0.29 mg/L, 0.27 mg/L, 1.46 mg/L and quantification limits of 0.96 mg/L, 0.94 mg/L, 4.92 mg/L for Pb, Cd and Zn respectively [70].

1.1.7. Simultaneous Determination of Pb, Cu and Zn

In water samples, ions of the metals Pb, Cu and Zn were simultaneously detected with the help of the anodic stripping square wave voltammetry. Multi-wall composite carbon nanotubes from polyaniline gold nanoparticles (AuNPs/PANI-MWCNTs) were used as electrochemical sensors and a 0.1 M acetate buffer with pH 5 as an auxiliary electrolyte. The method showed highly analytical characteristics as the LOD limits of the three ions were significantly below the guidelines set by the EPA namely 0.037 μg/L, 0.017 μg/L and 0.039 μg/L respectively [71].

1.1.8. Simultaneous Determination of Pb, Cd, Cu and Zn

Some papers deal with the simultaneous identification of all four heavy metals of interest. For this purpose, a lithographically printed carbon electrode with Bi and Hg (Bi/Hg-SPCE) has been formatted with 0.1 M acetate buffer and pH 4.5 in water samples. The sensor was disposable and showed the advantages of in-situ measurements, low cost, simple construction and multiple measurement capability. It also gave a wide cathode window, good electrochemical activity and high sensitivity for simultaneous analyte detection. The LOD limits were 0.082 μg/L, 0.16 μg/L, 0.64 μg/L, 0.97 μg/L and LOQ 0.27 μg/L, 0.52 μg/L, 2.14 μg/L, 3.22 μg/L for the metals Pb, Cd, Cu and Zn respectively [72]. A pencil graphite electrode molded with multiwall carbon nanotubes, Na-montmorilonite and Bi-nanoparticles (BiNP/MWCNT-NNaM/PGE) helped to detect the four heavy metals simultaneously, with a 0.1 M acetate buffer, pH 4.5 as the carrier electrolyte. The electrode gave a wide linear range, a reasonable detection limit (0.008 μM, 0.097 μM, 0.157 μM, 0.707 μM) and an acceptable quantification limit (0.03 μM, 0.32 μM, 0.52 μM, 2.36 μM). The structural and electrochemical characterizations of the BiNP/MWCNT-NNaM/PGE nanocomposite demonstrate a large surface area and low interfacial tension [73].

1.1.9. Simultaneous Determination of Pb and Other Heavy Metals

The lead cation has been detected along with some other metals in addition to those mentioned above, such as mercury (Hg), tellurium (Tl), cobalt (Co), and antimony (Sb).

In the simultaneous determination of Pb and Hg, techniques have been developed that utilize the square pulse anodic stripping. In one of these, a glassy carbon electrode formed with a Schiff base network (SNW_1/ GCE) is used as a working electrode and a 0.1 M KNO_3 and 0.01 M HCl solution was used as an electrolyte. The proposed sensor provided the advantages of simplicity, speed and low cost for the determination of metals in edible samples, with LOD levels equal to 0.00072 μmol/L and

0.01211 μmol/L for Pb and Hg respectively [74]. In soil and lake water samples, metals from an electrode shaped with multiwall carbon nanotubes and N,N′-di(salicylaldehyde)-1,2-diaminobenzene (BSD) (BSD/MWCNTs) were detected in a 0.1 M $NaNO_3$ solution. This technique exhibited high sensitivity, stability and reproducibility and the detection limits were low, 0.3 nM for Pb and 0.6 nM for Hg [75].

In different water samples (tap water, mineral water, wastewater) Pb ions were detected with the help of a glassy carbon electrode molded with Bi nanoparticles and dopamine polymer in multiwalled carbon nanotubes (BiNPs/MWCNTs-PDA/GCE). This electrode gave a wide range of concentrations, a low detection limit (0.07 μg/L) and good selectivity. The most important advantage of the proposed sensor is the modern detection of Tl^+ and Pb^{2+}in the presence of any heavy metals. The detection limit of Tl^+ is 0.04 μg/L [76].

In drinking water samples, simultaneous detection of ions of metals Pb, Cu and Co. This electrochemical analysis was performed using an EDTA-shaped carbon paste electrode (EDTA/CPE), with a square wave voltammetry. The technique is simple, fast and inexpensive. The electrode was shown to be linear in the concentration range from 0.302 mmol/L to 1.812 mmol/L for Pb under optimal chemical and electrochemical conditions and the LOQ and LOD limits for Pb are 7.77×10^{-9} mol/L and 2.33×10^{-9} mol/L respectively [77].

A 3D printed electrode molded with polylactic acid with graphene admixture was built to simultaneously detect traces of Pb and Sb metals in gunshot (GSR) samples. The LOD limit of Sb^{3+} is 1.8 μg/L and of Pb^{2+} 0.5 μg/L. The proposed sensor showed stable and repeated responses in different ratios of analyzers, good selectivity and high sensitivity. Furthermore, this work shows that this sampling and detection approach using the 3D printed G-PLA platform can be combined with a 3D-printed electrochemical cell and a portable potentiostat to serve forensic police experts [78].

1.1.10. Simultaneous Determination of Cd, Cu and Zn

A lithographically printed carbon electrode was molded with polyethylenimide, graphene oxide and graphite (PEI/GO/GRA/SPCE) for the simultaneous detection of ions of the metals Cd, Cu and Zn, by square pulse anodic stripping voltammetry. A buffer solution of 0.25 M acetate at pH 4.5 was used as electrolyte. According to the results, the proposed method showed sufficient LOD (0.53 μg/L, 1.52 μg/L, 0.23 μg/L respectively), sensitivity, selectivity and reproducibility for the detection of these metals in water samples [79].

1.1.11. Simultaneous Determination of Cd and Cu

For the simultaneous determination of the ions of the metals Cd and Cu, an electrode was formed with a poly(butylene-terephthalate adipate) copolymer and carbon nitrite dots (PBAT/CNDs) as well as a phosphate buffer 0.1 M, pH 3.0, as the carrier electrolyte. The method presented excellent electrochemical activity, showing low limits of LOD and LOQ. A linear behavior in the concentration range of 0.1 to 1.0 mM for Cd and Cu showed excellent sensitivity. The LOD and LOQ values obtained for Cd were 2.75×10^{-6} M and 9.16×10^{-6} M, and for Cu it was 7.09×10^{-6} M and 2.36×10^{-5} M, respectively [80].

1.2. Determination of Cd

The cadmium cation, Cd^{2+}, has been detected in a variety of samples, and one of them was the rice. In this study, a glassy carbon electrode with poly-L-tyrosine and bismuth, with the shape of buds (p-Tyr/Bi/GC), was formed and samples were studied with square pulse anodic stripping voltammetry. The preparation and testing of the membrane electrode composite showed good stability, repeatability and anti-interference capability. It was successfully applied in the determination of Cd, with a solution of 5.0 mmol/L KCl and 3.0 μmol/L Bi^{3+}, as the electrolyte, with satisfactory results according to those of the spectral method. The LOD limits for the metal were 0.11 nmol/L [81]. Two further studies were conducted to detect the Cd ion in water samples, with square pulse anodic voltammetry, acetate buffer and a glassy carbon electrode. In a study, this electrode was molded with MnO_2, Bi_2O_3 and graphene oxide (MnO_2/ Bi_2O_3/GO/GCE) giving a larger electrochemically active surface area and lower transportable charge resistance. This happened thanks to the strong synergistic effect between GO nanosheets and MnO_2/ Bi_2O_3 microspheres. The technique showed good repeatability, reproducibility and stability and the LOD limits were 0.22 μg/L [82]. In the other technique, the glassy carbon electrode was formed with a metallic organic frame of iron with amine (NH_2-MIL-53(Fe)/GCE) and gave LOD limits of 0.03 μM and LOQ of 0.09 μM, with the sensor showing good recoveries [83].

Another voltammetric technique used for the detection of cadmium is linear sweep stripping voltammetry (LSSV). In this method, a glassy carbon electrode was formed with 1,2-di-[o-aminothiophenyl]ethane (APTE-Mono@GCE) and analyzed in a 0.1 mol/L $LiClO_4$ solution. A stable and well-controlled electrograft process thus developed leading on a single-layer organic membrane, and gave low limits of detection for cadmium, 1.7 μg/L [84].

Successful determination of cadmium with high sensitivity has been also done by differential pulse voltammetry in seawater samples. The electrode used was a glassy carbon electrode formatted with nanoFe_3O_2, MoS_2 and Nafion (Nano Fe_3O_2/Mo S_2/Nafion/GCE), with simple operation, rapid response and high sensitivity. The linear relationship of Cd concentration was found in the range of 5-300 μg/L and the detection limit was 0.053 μg/L. Recovery of Cd in seawater ranged from 99.2 to 102.9 % [85]. A further determination of Cd in water samples (dam water, lake water, wastewater) was performed in a phosphate buffer, pH 5, by means of an organic metal frame and graphene oxide graphite rod electrode (GRE-ZIF-8/GO) and the differential pulse anodic stripping voltammetry. This technique exhibited high stability, speed and simplicity, good sensitivity and high reproducibility, with LOD limits equal to 0.03 μg/L [86].

The cadmium ion has also been determined concomitantly with mercury cations in drinking water samples, with a graphite- molded glassy electrode containing Se (Se-DG/GCE) and square pulse anodic stripping voltammetry. The electrode's ability to absorb cadmium and mercury makes it suitable for water purification purposes. Cd's LOD and LOQ limits are 1.9 μg/L and 6.3 μg/L, while Hg's are 4.3 and 14.3 μg/L [87].

1.3. Determination of Cu

Copper ions have been identified in drinking water samples, by square pulse anodic stripping voltammetry, with a selective ion Ca^{2+} electrode (Ca^{2+}- μISE) [88]. An amino acid containing organosilicate gel (3-mercaptopropyl)-trimethoxysilane gold electrode (APTES-PVP/MPTS/Au) was used to determine Cu in tap and lake water samples. A solution of 0.1 mol/L KCl, 2 mmol/L $[Fe(CN)_6]^{3-/4-}$ and 5 mmol/L $[Ru(NH_3)_6]^{3+}$ served as carrier electrolyte. Analysis of real samples proved that this electrode was favorable as a transducer platform for Cu^{2+} detection [89].

Differential pulse voltammetry was also used to detect Cu in drinking water, specifically cathodic differential pulse voltammetry. The working electrode was a carbon paste electrode molded with species of Mesorhizobium opportonistum bacteria that were first used in the production of a microbial biosensor (MOMB) [(MOMB)/UCPE] and the electrolyte was a 0.01M $HClO_4$ solution. MOMB has advantages for the determination of Cu(II), including good sensitivity and reproducibility, easy preparation, low cost, applicability to the sample, and no need for additional chemical processes. The LOD and LOQ limits were 2.0×10^{-8} M and 6.64×10^{-8} M respectively [90]. Another technique utilizing differential pulse anodic stripping voltammetry used a glassy electrode molded with Nafion solution, multiwall carbon nanotubes, and 1-butyl-3-methylimidazole hexafluorophosphate (MWCNTs-BMIMPF_6-Naf-GCE). Cu was detected with a 0.1 M acetate and chlorate buffer in juice and tea drinks. The molded electrode has strong anti-pollution properties and has the advantages of disposable design, low cost, renewability and excellent interference protection [91]. A pencil graphite electrode formatted with Cu^{2+} and cyclam (Cu(II)-modified PGE) was also used to detect Cu ions by anodic stripping adsorbtion voltammetry. The carrier electrolyte was a 1×10^{-3} mol/L $CuSO_4$, 1 mol/L H_2SO_4 sulphate buffer, while the LOD was calculated equal to 16 nmol/L. Cyclam chelate of bifunctional Ligand was shown to be highly Cu^{2+} selective compared to other divalent cations. The simplicity of preparation, the robustness of the covalent graft, the possible miniaturization of the system, the possibility of reusing the molded electrodes with one step ASV, the low risk of eutrophication and the low reagent consumption make this process very attractive for field measurements in both fresh water and marine environment [92]. In different water samples were determined copper ions using a magnetic carbon paste electrode (MCPE) and for this purpose L-cysteine functionalized core–shell Fe_3O_4@Au nanoparticles (Fe_3O_4@Au@L-cysteine). A phosphate buffer solution with pH 5.0 was used as the supporting electrolyte, and the results sawn that the method has satisfactory reproducibility and a low detection limit of 0.4 nM [93]

Simultaneous Determination of Cu and As

The simultaneous determination of copper and arsenic in water samples is vital to guarantee environmental and public health, being in agreement with regulations, and understanding the complex interactions between different contaminants in water systems.

The simultaneous detection of Cu^{2+} and As^{3+} ions was performed by square pulse anodic voltammetry using a gold nanostar electrode (AuNS-CSPE). A Britton-Robinson buffer solution was used as an electrolyte for this analysis and the results showed that this method provides excellent accuracy compared to GF-AAS in river water and tap water samples. The LOD limits for Cu are 42.5 μg/L while for As they are 2.9 μg/L [94]. Another technique involves a selective, stable and reproducible glassy carbon electrode molded with a new polymethyldopa-based nanocomposite along with gold nanoparticles immobilized on the surface of magnetic graphene oxide (GCE/GO/ Fe_3O_4@PMDA/AuNPs). The electrolyte used was a buffer solution of acetates (0.1 M, pH 6) and KCl 0.1 M. LOD levels were below acceptable limits and were equal to 0.11 μg/L and 0.15 μg/L for Cu and As respectively [95].

1.4. Determination of Zn

A boron impurity diamond electrode (BDD) was used to determine Zn^{2+} ions in pharmaceutical samples, by square pulse anodic stripping voltammetry, by batch injection in the analysis (BIA-SWASV). In this study, it was performed a simultaneous determination of zinc (Zn) and ascorbic acid (AA). The LOD and LOQ limits of Zn were 0.5 and 0.2 μmol/L and AA 5.4 and 17.8 μmol/L respectively. The proposed method exhibits high efficiency, sufficient selectivity, good accuracy, while requiring minimal sample preparation, small amount of reagents and sample volumes in each analysis. It has better limits of detection and does not require the use of an additional reagent to avoid interference of citrate (pharmaceutical excipient) in the determination of ions [96]. In Table I are being summarized the applications of voltammetry in the determination of heavy metals mainly in water samples.

Table 1. Applications of voltammetric analysis of heavy metals.

Metal	Technique	Electrode	Supporting Electrolyte	Type of sample	Limit of Detection (LOD)	Ref.
Pb^{2+}	ASV	Carbon e.Cu-shaped (Cu-CE)	0.01 M HCl + 1 M KCl	Drinking water, sewage	1 μM	[10]
	ASV	Glassy carbon e. formatted with eDAQ	1 M KNO_3	Tap water		[11]
	SWV	Carbon paste e. formed with geopolymer cement (CPE/GP- Dib_2)	0.2 M $NaNO_3$	Tap water, well and theral water	2.3×10^{-9} M	[12]
	SWASV	E. printed with ink injection printer and formatted with multiwall	0.1 M acetate buffer	Drinking water	1.0 μg/L	[13]

		carbon nanotubes (IJP-MW-CNT electrode)				
	SWASV	Lithographically printed e. Bi formatted and hierarchically tubular and porous biochar (Bi/PTBC800/SPE) (Bi/PTBC800/SPE)	acetate buffer (0.1 M, pH 4.5) + 500 μg/L Bi^{3+}	Water	0.02 μg/L	[14]
	SWASV	Lithographically printed e. carbon molded with dopamine polymer and polypyrolle hydrogel (PDA-PPy/SPCE) (PDA-PPy/SPCE)	HAc-NaAc PΔ (pH 4.5)	River water	0.15 μg/L	[15]
	SWASV	Glassy carbon e. formulated with Fe_3O_4 in a Schiff base network (Fe_3O_4@SNW_1 /GCE)	1.0×10^{-1} mol/L KNO_3	Food	0.95 nM	[16]
	SWASV	E. graphene oxide formulated with Bi and N	0.1 M, pH 4.5 acetate buffer	Tap water	10.9 pM	[17]
	SWASV	Glassy carbon e. formulated with Bi and Bi_2O_3 (Bi/Bi_2O_3@C/GCE)	0.1 M acetate buffer	Tap water, canal water, soil near a factory	6.3 nM	[18]
	SWASV	Glassy carbon e. molded with two-dimensional MXene with blue color (CoPB-MXene/GCE)	0.01 M, pH 6.5 phosphate buffer	Bottled water, tap water, lake water	0.97 nM	[19]
	LSASV	Coal paste e. molded with clay	0.1 M KCl	Water, biological water		[20]
	DPSV	Graphite-cork e.	0.5 M H_2SO_4, 0.1 M, pH 4.5 acetate buffer	Hair dye	1.06 μM (0.5M H_2SO_4), 1.26 μM (0.1 M acetate buffer, pH 4.5)	[21]
	DPASV	Glassy carbon e. molded with polypyrol, Bi film and metal organic frame (BF-PPy/UIO-66-NH_2/GCE)	0.5 mmol/L $K_3[Fe(CN)_6]$ + 1 mol/L KCl	Tap water, groundwater sample	0.05 μg/L	[22]
	DPASV	Glassy carbon e. molded with bismuth film, Nafion and a worm-like carbon structure with nitrogen admixture (Nafion-WNCF/ BFGCE)	0.1 M pH 4.5 acetate buffer + 1.4 mg/mLBi^{3+}	Lake water, tap water	0.2 μg/L	[23]

Pb^{2+}, Cd^{2+}	ASV	Hg film e. (MFE)		Coastal and transitional waters	4.0 ng/L , 0.50 ng/L	[24]
	ASV	Hanging Hg drop e. (HMDE)	9.00 mL model brine	Brine		[25]
	ASV	Cu film e. (CuFE)	0.1 M HCl + 0.4 M NaCl	Tap water	0.6 µg/L, 1.8 µg/L	[26]
	SWV	Carbon paste e. formatted with Bi film (BiFE-CPE)	0.01 M, pH 4.6 acetate buffer	Water	0.3 µg/L , 0.5 µg/L	[27]
	SWASV	Lithographically printed e. based on graphite and covered with Nafion	acetate buffer 50 mM + NaCl 50 mM pH 4.6	Spring water, sea water		[28]
	SWASV	Carbon paste e. molded from multiwall carbon nanotubes and antimony trioxide (Sb_2O_3/CNTCPE)	0.01 M HCl	Tap water	1.2 µg/L, 1.7 µg/L	[29]
	SWASV	Lithographically printed black carbon e. with poly(propyleneimine) (SPE-CB-PPI)	acetate buffer 0.1 M, pH 4.6	Tap water	3.6 µg/L, 15.3 µg/L	[30]
	SWASV	Glassy carbon e. formulated with a reduced graphene oxide nanocomposite decorated with $[(BiO)_2CO_3$ and Nafion $[(BiO)_2CO_3$-rGO-Nafion/GCE]	3 M KCl	Water	0.24 µg/L, 0.16 µg/L	[31]
	SWASV	Polythionine- molded glassy carbon e. (in the presence of Bi) and multi-wall carbon nanotubes (Bi-PTH/MWCNTs/ GCE)	0.1 M, pH 3.5 acetate buffer	Water	0.4 nM, 0.6 nM	[32]
	SWASV	Glassy carbon e. formulated with carbon combined with N, and Ti_3C_2-MXene (Ti_3C_2@N-C/GCE)	5 mM $[Fe(CN)_6]^{3-/4-}$ solution + 0.10 M KCl	Sea water, tap water	1.10 nM , 2.55 nM	[33]
	SWASV	Carbon e. molded with Hg	0.1 mol/LHCl	Vegetable oil	0.01 µg/kg, 0.06 µg/kg	[34]
	SWASV	Glassy carbon e. formulated with nanoporous Bi, superficially decorated with Bi_2O_3 (Bi_2O_3@NPBi/GCE)	0.1 M, pH 3.0–5.5,acetate buffer	Tap water	0.02 µg/L , 0.03 µg/L	[35]

	SWASV	E. formulated with salicylidene-2-amino benzyl alcohol and multiwall carbon nanotubes (SABA/MWCNTs electrode)	0.1 M acetate buffer	Rice water, tobacco extract, raw milk	0.012 ng/L, 0.02 ng/L	[36]
	SWASV	Lithographically printed e. formatted with Nafion	0.1 M PΔ NaAc-HAc	Sewage	8.4 µg/L, 0.032 mg/L	[37]
	DPASV	Lithographically printed e. bismuthene- molded two-dimensional carbon (2D Bi$_{exf}$–SPCE)	0.1 mol/L acetate buffer (pH 4.5)	Certified estuarine water samples	0.06 µg/L, 0.07 µg/L	[38]
	DPASV	Glassy carbon e. molded with silane bentonite decorated with Ag nanoparticles (AgNP@Bt/ TC/GCE)	5.0 mg/L σε 0.1 mol/L acetate buffer (pH 4.0)	River water	0.88 µg/L, 0.79 µg/L	[39]
	DPASV	Glassy carbon e. molded with polyrutin and Ag nanoparticles (polyrutin/AgNPs/GC)	0.1 M, pH 5 acetate buffer	Tap water, soil sample, hair	3 nM, 10 nM	[40]
	DPASV	Polypyrol- molded pencil graphite e., and CO$_2$ (PPy-CO$_2$@PGE)	0.1 M acetate buffer	Natural water	0.018 nM, 0.023 nM	[41]
	DPASV	Glassy carbon e. formulated with Sb and Bi (Sb/Bi-GCE)	0.1 M, pH 4.5 acetate buffer	CRM soil sample, tap water	0.01 µg/L , 0.5 µg/L	[42]
	DPASV	Glassy carbon e. formulated with Nafion and Bi nanoplates (Nafion/BiNP/GCE)	0.1 M, pH 4.5 acetate buffer	Tap water, sewage	0.178 nM, 0.376 nM	[43]
	DPASV	Lithographically printed e. two-dimensional microfiber molded with Sb (2D Sb$_{exf}$-SPCNFE)	0.01 mol/L, pH 2 HCl	Certified estuarine water	0.1 µg/L, 0.9 µg/L	[44]
	DPSV	Glassy carbon e. rotating disc molded with Sb (Sb-GC-RDE)	0.01 M HCl	Soil water, soil	1.1 µg/L, 1.4 µg/L	[45]
	DPASV	Glassy carbon e. molded with carbon black and polyriboflavin in the presence of Bi (Bi-PRF/CB/GCE)	0.1 M, pH 4.5 acetate buffer	Rice, honey, vegetables	0.13 nM, 0.16 nM	[46]
	DPAdSV	Carbon paste e. molded with charcoal (BC-CPE)	0.1 mol/L, pH 4.8 acetate buffer	Samples of biochar (charcoal) from coffee tree husks	0.2 µg/L, 1.7 µg/L	[47]

	SWASV	Glassy carbon e.molded with Bi (Bi/GCE)	0.2 M, pH 5.0 acetate buffer	Soil		[48]
	SWASV	Glassy carbon electrode (GCE) coated with poly(amidoamine) dendrimer functionalized magnetic graphene oxide (GO-Fe_3O_4-PAMAM)	0.1 M acetate buffer	Water	130 ng/L, 70 ng/L	[49]
Pb^{2+}, Cd^{2+}, Hg^{2+}	ASV	3D printed e. graphene/polylactic acid	1 mM διάλυμα από FcMeOH + 0.5 M KCl ως φέρων ηλεκτρολύτης	Tap water	Hg: 6,1 nM	[50]
	DPSV	Nanoel. Molded with Au		Liquid foods (cow's milk, orange juice, apple juice)	1.0 μg/L, 1.1 μg/L, 1.2 μg/L	[51]
	DPASV	Carbon paste e. formulated with Na_2CO_3 and active Hordeum vulgare L powder (HVW-Na_2CO_3/CPE)	Όξινα διαλύματα (0.1 M HCl)	River water, tap water	0.0691 nM, 1.82 nM, 0.237 nM	[52]
Pb^{2+}, Cu^{2+}	ASV	Glassy carbon e. formulated with Nafion, and $MnCo_2O_4$ (Nafion/$MnCo_2O_4$/GCE)	HCl/KCl (0.1 mol/dm^3)	Wine	1.67 μg/dm^3, 7.14 μg/dm^3	[53]
	ASV	High-Content Hydroxyapatite Carbon (Hap/CE)	0.1 M KNO_3	Water		[54]
	SWSV	Glassy carbon e. molded with multiwall carbon nanotubes, Nafion and ZIF-67 (ZIF-67/MWCNT/Nafion-GCE)	0.1 M pH 2.0 HAc-NaAc	Water from Changchun's Sanjia and Yan lakes	1.38 nM, 1.26 nM	[55]
	SWASV	Graphite e. formulated with caffeic acid [GE/poly(CA)]	1.0 M HNO_3	Samples of artisanal sugar cane spirit	3.01 μg/L, 4.50 μg/L	[56]
Pb^{2+}, Cd^{2+}, Cu^{2+}	SWV	Carbon paste e. molded with Bigarreau Burlat shell core (BBKS-CPE)	acetate buffer (0.2 M)	Tap water, sea water, industrial wastewater	8.48 μg/L, 9.56 μg/L, 9.77 μg/L	[57]

	SWSV	Microgel. molded with high-density carbon nanotube fiber rods (HD-CNTf)		Tap water	-0.45 nM (92 ng/L) , 0.26 nM (55 ng/L) in simulated drinking water -0.24 nM (27 ng/L) in tap water, 0.25 nM (28 ng/L) in simulated drinking water -6.0 nM, (376 ng/L) in tap water, 0.32 nM (20 ng/L) in simulated drinking water	[58]
	SWASV	Antifouling microelectrode arrays integrated in gel (GIME)			1 ng/L, 0.7 ng/L, 6.6 ng/L	[59]
	SWASV	Glassy carbon e. molded with Fe$_3$O$_4$ and D-valine (Fe$_3$O$_4$-D-Val/GCE)	0.1 M acetate buffer	Water	18.89 nM, 18.38 nM , 7.481 nM	[60]
	SWASV	Glassy carbon e. molded with nanostructure ZnO and Nafion (ZnO-NP-Nafion/GCE)	0.1 M KCl + 5 mM [Ru(NH$_3$)$_6$]$_3$	Water	11.88 nM, 16.21 nM, 47.33 nM	[61]
	DPASV	Hanging Drop Hg e. (HDME)	KCl 0.5 M, pH 6.0	Water		[62]
	DPASV	Biochar e. in a metal form molded with B (B-bioC/MEDs)	0.1 M acetate buffer	Rural irrigation water	4 nM, 54 nM, 24 nM	[63]

Pb^{2+}, Cd^{2+}, Cu^{2+}, Hg^{2+}	DPASV	Lithographically printed e. carbon formulated with nanoparticles Ag (AgNS/SPCE)	1 M, pH 4.4 acetate buffer	Tap water, rainwater, lake water	2.5 μg/L, 0.4 μg/L, 0.73 μg/L, 0.7 μg/L	[64]
	DPSV	Magnetic glassy carbon e. molded with Fe$_3$O$_4$ and silica (Fe$_3$O$_4$@SiO$_2$/MGCE)	1 M, pH 5 acetate buffer	Milk	16.5 nM, 56.1 nM, 79.4 nM, 56.7 nM	[65]
Pb^{2+}, Cd^{2+}, Zn^{2+}	ASV	Polymeric e. loaded with carbon fiber embedded in plastic fluid base	0.10 mol/L acetate buffer	Fish feed		[66]
	SWASV	Pencil graphite e. molded with multiwall carbon nanotubes and Bi (MWCNT/Bi/PGE)	pH 4.5 acetate buffer	Water	0.27 μg/L, 0.43 μg/L, 1.63 μg/L	[67]
	SWASV	Lithographically printed carbon e. formulated with poly(3,4-ethylenedioxythiophene) fibers with polyvinyl alcohol aqueous solution and nanoparticles Ag (PEDOT/PVA/AgNPs fibers-modified SPCE)	0.1 M, pH 4.6 acetate buffer	Drinking water	8 μg/L, 3 μg/L, 6 μg/L	[68]
	SWASV	Carbon paste e. molded with CuO and TbFeO$_3$ (TbFeO$_3$/CuO/CPE)	acetate buffer pH 4.8	Pasteurized milk, apple juice, drinking water	0.12 mg/L, 0.29 mg/L, 0.48 mg/L	[69]
	SWASV	Carbon paste e. molded with Bi and Sb (Bi–Sb/CPE)	acetate buffer pH 5.6	Water	0.29 mg/L, 0.27 mg/L, 1.46 mg/L	[70]
Pb^{2+}, Cu^{2+}, Zn^{2+}	SWASV	Multiwall Composite Carbon Nanotubes from Gold Nanoparticles with Polyaniline (AuNPs/PANI-MWCNTs)	0.1 M, pH 5.0 acetate buffer	Water	0.037 μg/L, 0.017 μg/L, 0.039 μg/L	[71]
Pb^{2+}, Cd^{2+}, Cu^{2+}, Zn^{2+}	SWASV	Lithographically printed e. carbon molded Bi and Hg (Bi/Hg–SPCE)	1.0 M, pH 4.5 acetate buffer	Surface water	0.082 μg/L, 0.16 μg/L, 0.64 μg/L, 0.97 μg/L	[72]
	SWASV	Pencil graphite e. molded with multiwall carbon nanotubes, Na-montmorilonite and Bi	0.1 M, pH 4.5 acetate buffer	Tap water	0.008 μM, 0.097 μM, 0.157 μM, 0.707 μM	[73]

		nanoparticles (BiNP/MWCNT-NNaM/PGE)				
Pb^{2+} and other metals	SWV	Glassy carbon e. molded with Schiff base network (SNW$_1$/ GCE)	0.1 M KNO_3 + 0.01 M HCl	Edible samples	0.00072 µM	[74]
	SWASV	E. molded with multiwall carbon nanotubes and N,N′-di(salicylaldehyde)-1,2-diaminobenzene (BSD) (BSD/MWCNTs)	0.1 M $NaNO_3$	Lake water, soil sample	0.3 nM	[75]
	SWASV	Glassy carbon e. molded with Bi nanoparticles and dopamine polymer in multiwall carbon nanotubes (BiNPs/MWCNTs-PDA/GCE)	0.1 M, pH 5 acetate buffer	Tap water, mineral water, sewage	0.07 µg/L, Tl^+: 0.04 µg/L	[76]
	SWV	Carbon paste e. molded with EDTA (EDTA/CPE)	0.1 mol/L NaCl	Drinking water	2.33 nmol/L	[77]
	SWASV	3D printed e. using polylactic acid with graphene admixture	0.01 mol/L HCl	Gunshot samples (GSR)	0.5 µg/L	[78]
Cd^{2+}, Cu^{2+}, Zn^{2+}	SWASV	Lithographically printed e. carbon molded with polyethyleneimide, graphene oxide and graphite (PEI/GO/GRA/SPCE)	0.25 M, pH 4.5 acetate buffer	Water	0.53 µg/L, 1.52 µg/L, 0.23 µg/L	[79]
Cd^{2+}, Cu^{2+}	SWV	E. formulated with poly(butylene-terephthalate adipate) copolymer and carbon nitrite dots (PBAT/CNDs)	0.1 M, pH 3.0 phosphate buffer	Tap water	2,7 µM (Cd), 7.09 µM (Cu)	[80]
Cd^{2+}	SWASV	Glassy carbon e. molded with poly-L-tyrosine and bismuth reminiscent of buds (p-Tyr/Bi/GC)	5.0 mmol/L KCl + 3.0 µmol/L Bi^{3+}	Rice	0.11 nM	[81]
	SWASV	Glassy carbon e. molded with MnO_2, Bi_2O_3 and graphene oxide (MnO_2/Bi_2O_3/GO/GCE)	0.1 M acetate buffer	Water	0.22 µg/L	[82]
	SWASV	Glassy carbon e. formed with metal organic frame iron with amine (NH_2-MIL-53(Fe)/GCE)	acetate buffer	Water	0.03 µM	[83]

	LSSV	Glassy carbon e. formulated with 1,2-di-[o-aminothiophenyl (APTE-Mono@GCE)	0.1 mol/L $LiClO_4$	Real samples	1.7 µg/L	[84]
	DPV	Glassy carbon e. molded with nano-Fe_3O_2, MoS_2 and Nafion (Nano-Fe_3O_2/MoS_2/Nafion/GCE)	0.1 mol/L, pH 4.2 acetate buffer	Sea water	0.053 µg/L	[85]
	DPASV	Graphite rod e. molded with organic metal frame and graphene oxide (GRE-ZIF-8/GO)	phosphate buffer pH 5.0	River water, dam water, sewage	0.03 µg/L	[86]
	SWASV	Glassy carbon e. molded with graphite containing Se (Se-DG/GCE)	1 M phosphate buffer	Drinking water	1.9 µg/L, Hg: 4.3 µg/L	[87]
Cu^{2+}	SWASV	Selective Ca^{2+} ion (Ca^{2+}-µISE)	0.1 M acetate buffer	Drinking water	1 µM	[88]
	SWSV	Gold e. with (3-mercaptopropyl)-trimethoxysilane formulated with microfibers organosilicate gel containing amino acid (APTES-PVP/MPTS/Au)	0.1 mol/L KCl solution + 2 mmol /L $[Fe(CN)_6]^{3-/4-}$ + 5 mmol/L $[Ru(NH_3)_6]^{3+}$	Tap water, lake water	2.6 pM	[89]
	DPCSV	Carbon paste e. molded with biosensor Mesorhizobium opportonistum. [(MOMB) / UCPE]	0.01M $HClO_4$	Drinking water	2.0×10^{-8} M	[90]
	DPASV	Glassy carbon e. molded with Nafion solution, multiwall carbon nanotubes and 1-butyl-3-methylimidazole hexafluorophosphate (MWCNTs-BMIMPF6-Naf-GCE)	0.1 mol/L PΔ HAc-NaAc + 0.1 mol/L KCl	Juice and tea drinks	16 µg/L	[91]
	AdASV	Pencil graphite e. formatted with Cu^{2+} and cyclam (Cu(II)-cyclam-modified PGE)	$1x10^{-3}$ mol/L $CuSO_4$ / 1 mol/L H_2SO_4	Sea water	16 nM	[92]
	DPV	Magnetic carbon paste electrode (MCPE), L-cysteine functionalized core–shell Fe_3O_4@Au nanoparticles (Fe_3O_4@Au@L-cysteine)	Phosphate buffer, pH 5.0	Water	0.4 nM	[93]
	SWASV	Nanostar gold e. (AuNS-CSPE)	Britton-Robinson PΔ	River water, tap water	42.5 µg/L, 2.9 µg/L	[94]

Cu^{2+}, As^{3+}	SWASV	Glassy carbon e. with a new polymethyldopa-based nanocomposite material together with gold nanoparticles immobilized on the surface of magnetic graphene oxide (GCE/GO/Fe_3O_4@PMDA/AuNPs)	0.1 M acetate buffer (pH 6.0) + 0.1 M KCl	Drinking water, pool water	0.11 µg/L, 0.15 µg/L	[95]
Zn^{2+}	Batch Injection Analysis (BIA)-SWASV	Diamond e. with boron admixture (BDD)	Britton-Robinson (BR) PΔ 0.04 mol/L	Pharmaceutical samples	0.2 µM	[96]

2. Conclusions

A literature review was performed regarding the determination of heavy metals, mainly in water samples. Voltammetric techniques provide fast and reliable results, they have low cost, they are simple to apply, repeatable and they also have great sensitivity and selectivity. The most common techniques used to determine heavy metals are differential pulse voltammetry (DPV), square wave voltammetry (SWV) and anodic stripping voltammetry (ASV). The most commonly used electrodes were modified carbon paste and glassy carbon.

The application of voltammetric techniques in the determination of heavy metals in water samples is an issue of great importance while the developed analytical analytical methods have shown selectivity and low detection limits. Electrochemical techniques offer an important advantage in the analysis of heavy metals while the development of new and selective electrode surfaces and electrochemical detectors will enhance analytical figures of merit .

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