

ELECTROCHEMICAL RESEARCH OF BIORELEVANT ORGANIC COMPONENTS AND HEAVY METAL IONS IN MEDICINAL PLANTS EMPLOYING CARBON PASTE ELECTRODE

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ABSTRACT

Based on the voltametric response at a carbon paste electrode modified with carbamoyl phosphonic acid (acetamide phosphonic acid) self-assembled monolayer (SAM) on mesoporous silica (Ac-Phos SAMMS), a new sensor was developed for the simultaneous detection of cadmium (Cd^{2+}), copper (Cu^{2+}), and lead (Pb^{2+}). The metal ions are first preconcentrated onto Ac-Phos SAMMS in an open circuit, after which the species are electrolyzed and the potential is swept to positive values using a square wave. The process of preconcentration and the variables that impact it were studied. The voltametric responses linearly rose from 10 to 200 ppb metal ion concentration or 1 to 30 minutes of preconcentration period. In the pH range of 2–6, the responses likewise developed in the same way as the adsorption isotherm. After 2 minutes of preconcentration, the metal detection limits were 10 ppb, but after 20 minutes, they dropped to 0.5 ppb.

KEYWORDS: *Self-assembled monolayer; Chemically modified electrode; Carbon paste electrode*

INTRODUCTION

Collection of liquid discrete samples for subsequent laboratory analysis using methods like ICP-MS and AAS is the current gold standard for heavy metal quantification at underground hazardous waste sites. Long waiting periods are common for findings from government or private laboratories located far away. Time and money spent on characterizing and treating hazardous waste sites may be cut in half with the use of sensors that can obtain ppb-level heavy metal concentrations in real time. The use of stripping voltammetry-based electrochemical sensors to measure heavy metal content in water shows promise. Sensitive, small, cheap, and simple to include into field-deployable systems, these sensors are becoming increasingly popular. Preconcentration of metal ions at an electrode surface is a common step in stripping voltammetry for trace metal ions, followed by measurement of the accumulated species using voltammetric techniques. Mercury drop or mercury film electrodes have allowed for the preconcentration of metal species for decades. Mercury drop electrodes are less preferable than solid-state sensors in everyday field applications due to their mechanical instability during the test process.

The usage and disposal of harmful mercury also present problems for mercury-based electrodes. However, in adsorptive stripping voltammetry (AdSV), metal ions are accumulated on the electrode through ion

exchange or chelation without the application of a potential by means of preconcentration at an electrode modified with functional ligands. This method has a number of advantages beyond not requiring a solid-state or mercury: it can preconcentrate metal ions that cannot be reductively electrolyzed; electrolytes are not required in the preconcentration solution, which lowers the potential for introducing contaminants or competing ligands; and, with the right ligand, the overall selectivity of the analysis for the targeted metal ions may improve. Adsorption of monolayers of host molecules (e.g., functionalized self-assembled monolayers (SAMs) and polymeric films) on the electrode surfaces or embedding of appropriate functional ligands in a conductive porous matrix are two methods for creating electrodes for AdSV for trace metal ions. It's possible that SAM thin films have poor stability and endurance and a low number of functional groups.

Although polymeric films are more stable and durable than SAM thin films, changes in solution pH or electrolyte concentration can cause the films to expand and shrink, causing detection delays and lower electrode activity. Trace metals are often preconcentrated and quantified using carbon paste electrodes modified with functional ligands. These sensors rely on ligands to detect changes in electrical potential, however the ligands only loosely associate with or touch the electrode. Therefore, the modifiers must be insoluble in the solvents in order to prevent the sensor's performance from degrading over time due to a lack of ligand-bearing material. Chemical functionality can be maintained despite diffusion or abrasive wear by first covalently bonding the ligands to high surface area substrates (such porous silica) and then embedding them into the carbon graphite matrix. Walcarius et al. have employed polysiloxane-immobilized amine and aminopropyl-grafted silica as electrode modifiers to investigate copper(II) absorption from water.

Amorphous materials (such as silica gel) with a tortuous structure might impede the diffusion of target analytes to the binding sites during the preconcentration step. Easy access to the binding sites is a crucial aspect of the electrode modifications, since such diffusion is often the rate-determining step in the voltammetric studies that rely on porous materials as electrode. This is why well-ordered, hexagonal porous silicas (MCM-41) have recently been used as a substrate for immobilization of basic functional groups such as amine and thiol. Mercury is used as a typical metal ion, however the metrological characteristics of adsorptive stripping voltammetry have not yet been explored in relation to functionalized amorphous silicas vs functionalized MCM-41 as electrode modifiers.

This study details the use of an MCM-41 electrode modified with a self-assembled monolayer for the simultaneous detection of hazardous metal ions. Self-assembled monolayer on mesoporous supports (SAMMS) are a novel type of nanoengineered sorbent that have been developed at PNNL. The interfacial chemistry of these nanoporous hybrid materials may be tailored to preferentially sequester any given target species, making them very effective sorbents. The schematic of SAMMS with acetamide phosphonic acids as terminal groups is displayed on the surface of the successful material acetamide phosphonic acid self-assembled monolayer on mesoporous. The nominal pore size of the mesoporous silica (MCM-41) was 5.0 nm, and its surface area was 989 m²/g. MCM-41's large surface area and the monolayer structure.

Population increase, agricultural operations, and the quick development of continuously releasing heavy metals into the surroundings have all contributed to a significant problem all over the world in the form of environmental pollution in recent decades. The ability of toxic metal ions to accumulate in human organs makes them a major environmental concern, and so does the need for highly selective, sensitive, and rapid monitoring methods. Toxic heavy metal ions have a significant impact on the environment, and their presence

in water near chemical industries is a growing industrial issue. The plastics business, coating technology, and the battery industry are just a few of the many industrial sectors that rely heavily on cadmium.

It is also the primary waste product from zinc production. Cadmium is a heavy metal that can cause a wide range of adverse health effects when it accumulates in living organisms, including muscle cramps, renal deterioration, erythrocyte destruction, nausea, diarrhea, salivation, and chronic pulmonary fibrosis. Recent studies have shown that this contributes to a cancerous condition. Recently, there has been a lot of focus on developing a reliable analytical method for measuring extremely low levels. Inductively coupled plasmaatomic emission and X-ray spectroscopy are two of the most trusted and precise analytical methods for determining trace levels, although other techniques have also been used. However, there are significant drawbacks to using these analytical methods, such as their high cost, high levels of tediousness, and lengthy execution times.

Not only are they not suitable for on-site evaluation, but a wide range of laborious Voltammetric methods have replaced these other approaches because of their superior sensitivity, selectivity, speed of analysis, simplicity, portability, low cost, and ease of maintenance; they are also inexpensive and can be used for speciation. Due to their easily regenerated surface, low cost, simplicity of modification, low background current, high sensitivity, and selectivity of electrochemical methods, chemically modified carbon paste electrodes (CMCPEs) have found widespread use in modern metal ion analysis. The processes by which electrodes do their job are sensitive to the specifics of the modifications used. Carbon electrodes are often modified using a wide variety of modifiers, including as organic ligands, polymers, ion exchangers, and nanomaterials. Because of their unique complexing capacity with metal ions, ligands modified carbon paste electrodes (CPEs) have been used in the electrochemical detection of hazardous metal ions. Most chelating ligands include acidic groups like COOH or SH or OH or neutral donating groups like N or O that may combine with metal ions to create stable complexes.

OBJECT

1. The use of a carbon paste electrode to analyze heavy metal ions in herbal remedies
2. The research One such method is known as adsorptive stripping voltammetry (AdSV), which

RESEARCH METHODOLOGY

Paraffin oil cadmium standard solution and spectroscopic-grade graphite powder (BDH Laboratory Supplies Poole, England) were used in this research. Distilled water, phosphoric acid (Riedel-de Haen acetic acid (Sigma-Aldrich, USA), and boric acid Reagents, were used to create Britton Robinson (B-R) buffers of varying concentrations. The pH of the B-R solution was altered by adding 0.1 M sodium hydroxide solution to get the desired range of values. Standard solutions for use in optimization experiments were prepared using sodium acetate, ammonium chloride, sodium perchlorate, hydrochloric acid, sodium phosphate (BDH Chemicals Ltd, England), and sodium citrate/citric acid. Sodium sulfate (AnalaR), sodium chloride (Aldrich Chemical Co. Ltd Gillingham Dorset, England), magnesium chloride (BDH Chemicals Ltd Poole, England), calcium nitrate (Aldrich Chemical Co. Ltd Gillingham Dorset, England), potassium nitrate (BDH Chemicals Ltd Poole, England), cupric nitrate (AnalaR), lead nitrate (BDH Chemicals Ltd Poole, England),

Actual samples were digested using 30% hydrogen peroxide and 68% nitric acid. For the purpose of deaerating test solutions, 99.999% pure Argon from Merck-Schuchardt was employed. Electrode morphological characterizations were evaluated using a scanning electron microscope (Cx-200 COXEM, Korea) after HDPBA was produced by reacting N-phenylhydroxylamine with N-phenylbenzimidoyl chloride at 0° C in ether. The FTIR spectra were recorded with a spectrometer that uses the Fourier transform of infrared light (PerkinElmer, Spectrum The PerkinElmer Lambda 950 UV/Vis/NIR equipment was used for the UV-Vis analysis. The CHI 840C electrochemical analyzer (CHI instruments, USA) was used for the electrochemical measurements. All voltammetric measurements were performed using an electrode system consisting of a working electrode (either modified or unmodified CPE), a reference electrode (Ag/AgCl), and a counter electrode (Pt-wire). As the container for the answer, a 20 mL cell was utilized.

The solutions' pH levels were measured with a pH meter (sensION, China), and the time and temperature were monitored with a stopwatch and a magnetic stirrer. Cd(II) concentrations were determined using a graphite furnace atomic absorption spectrometer (Agilent 280Z AA Zeeman, GTA120, USA) for atomic spectrometric analysis. The Preparation of Electrodes 2.2. Using a mortar and pestle, we blended together 0.05 g of the modifier (HDPBA), 0.95 g of graphite powder (spectroscopic grade, BDH Laboratory Supplies Poole, England), and 0.36 mL of paraffin oil (Uvasol Merck, Germany) to create modified CPE. The paraffin oil was utilized to bind the powder and the HDPBA into a consistent paste, and it does not dissolve the modifier paraffin oil in the combination. Because of this, the HDPBA had not liquefied in the carbon paste. was ground for 20 minutes before being put into a plastic syringe (1 mL) with a 3 mm outside diameter to serve as an electrode, with a Cu wire leading to a measuring device. The production of CPE was identical other from the absence of the HDPBA modification. In order to refresh the electrode, a tiny section of the electrode's surface was scraped off and a new paste applied in its place.

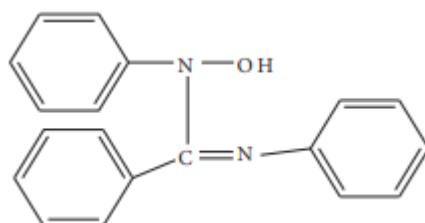


Figure 1: Structure Of N1 -Hydroxy-N1 ,N2 -Diphenyl Benzamidine (HDPBA).

VOLTAMETRIC DETERMINATIONS

The below procedures were used to make voltammetric determinations using CV and SWASV: First, 0.1 M B-R buffer (pH 4) containing the accumulation solution was injected into the cell, and then a known amount of Cd(II) was added. This is the accumulation stage. After placing the electrodes in the cell and applying a potential of 1.00 V for a set period of time while swirling the solution, Cd(II) was preconcentrated at the electrodes' surface. Following preconcentration, the solution was allowed to rest for 10 s in order to stabilize and reduce background current. Cd(II) evoltammograms were collected during a positive potential scan from 1.2 to 0.2 V vs Ag/ AgCl, which is step (b) of the stripping procedure. For each measurement, we ran 4–5 scans over the electrode with 0.1 M B–R solution to clean it. To avoid any possible accumulation in the cell, a new buffer solution was used for each measurement. Purifying the test solution with argon for varying

periods (zero, five, eight, and ten minutes) allowed researchers to examine the impact of deaeration on Cd(II) peak currents.

REAL SAMPLES ANALYSIS

Under optimum experimental conditions, the suggested electrode was used to quantify Cd(II) in tobacco samples and five different types of environmental water samples, including industrial effluent, bottled water, well water, and stream water. The water samples were filtered beforehand so that no solids would be included in the analysis. Voltammetric readings were taken to assess the pH levels after they were all adjusted to a value of 4. Each water sample used in the recovery trials had a known concentration of Cd(II) added to it. The GFAAS technique was also used to ascertain the presence of Cd(II) in the collected water samples. Ten local cigarettes were sampled for their tobacco, which was then dried in a 105°C oven and crushed. Powdered samples weighing 500 mg were added to the digestion vessel, together with 5.0 mL of H₂O₂ (30%) and 3.0 mL of concentrated HNO₃. This was done so that the concentration of cadmium(II) could be determined. The vessel was sealed, then rotated for eight minutes in the oven's carousel. The digest was almost completely evaporated. The residue was dissolved with HNO₃, and the solution was filtered and pH-adjusted for voltammetric measurement.

DATA ANALYSIS

CHARACTERIZATION OF THE DEVELOPED ELECTRODES

The FT-IR, UV-Vis, and SEM methods were used to conduct spectrum analysis of the modifier (HDPBA) and morphological characterisation of unmodified CPE and HDPBACPE, respectively. In order to chemically characterize the modifier (HDPBA) as well as the unmodified and modified CPEs, Fourier transform infrared (FTIR) analysis was used. Both the HDPBA-modified graphite and the unmodified graphite were characterized by FTIR after being prepared by combining the two powders in a mortar and pestle without the addition of paraffin oil. First, using a mortar and pestle, the HDPBA and graphite powder were thoroughly combined. One milligram of graphite powder (for unmodified paste) and one milligram of graphite powder plus the modifier, HDPBA (for modified paste), were each combined with around 100 milligrams of KBr powder in a mortar and pestle before spectra were acquired. The pellet was formed by compressing the paste. The reference spectra was obtained from a KBr pellet. The PerkinElmer used to record the FTIR spectra has a resolution of 1 cm⁻¹ over the range of 4500 to 500 cm⁻¹ in the wave number. The spectrum of the modifier (HDPBA) was measured from 4500 to 500 cm⁻¹ using FTIR, as were those of the modified and unaltered CPEs. shows that in the original graphite spectrum (spectrum a), there are no significant bands.

Bands at 1030, 1435, 1575, 1640, 3000, and 3400 cm⁻¹ were seen in the HDPB A graphite mixture (spectrum b), which are diagnostic of the stretching of NO, CN, C CH(aromatic, stretching), and OH bonds in the ligand chemical structure. are in agreement with the aforementioned published works Spectral evidence confirmed the addition of HDPBA to the customized electrode. The modifier's spectra were captured in ethanol. free modifier (HDPBA) demonstrated congruence with prior research findings. After Cd(II) was added to the modifier, the spectra exhibited a bathochromic shift (max (ethanol) = 334), which is indicative of complex formation with the analyte. Research into the produced electrodes' surface properties The surface morphologies of HDPBA were seen to differ significantly in SEM pictures. When comparing the surfaces of

modified and unmodified CPE, Figure 4(a) shows that the unmodified surface is dominated by a uniformly distributed and homogeneous surface with small pores; however, after modification, the numbers and pore sizes were much larger, and their distribution on the electrode surface became uneven due to the addition of the ligand into the paste, making it favorable for the adsorption of Cd(II) on the electrode surface and resulting in better sensing.

Analysis of Electrochemical Properties. Characterizations by CV and electrochemical impedance spectroscopy (EIS) in KCl solution were used to compare the electrochemical behaviors of the unmodified carbon paste electrode and HDPBACPE. ferricyanide cyclic voltammograms (CVs) are displayed for both the original and altered electrodes in The unaltered carbon paste electrode showed very strong redox peaks (peak a). The peak currents were reduced and the peak b potential values were significantly different when the HDPBA modified electrode was used. that HDPBA is successfully incorporated on the carbon paste electrode surface because ferric cyanide ions are repelled by the lone pair electrons of OH and N in HDPBA. This causes the ligand to act as a blocking layer for mass and electron exchange, preventing from migrating towards the electrode surface. When looking at the electrochemical properties of an electrode's surface, EIS is a crucial instrument. Charge transfer resistance (Rct), double layer capacitance (Cdl), electrolyte resistance (Rs), and impedance (Zw (W)) are all EIS parameters. Charge transfer resistance (Rct) is a key metric that may be used to describe the electrode interface qualities, along with the others stated. impedance diagram with a semicircle at Rct.

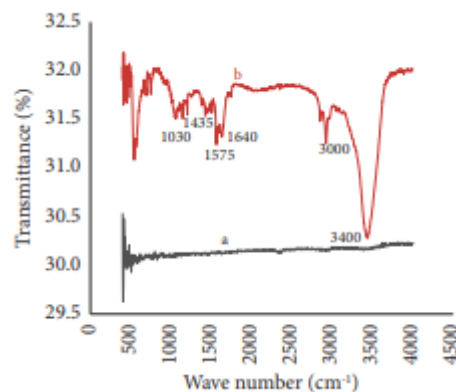


Figure 2: FT-IR Spectra of Unmodified Graphite (A) And HDPBA Modified Graphite (B).

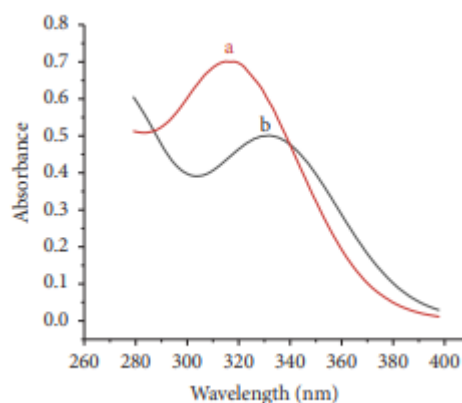


Figure 3: UV Spectra Of 60 μm HDPBA In Ethanol (A) In the Absence of Cd (II) And (B) In the Presence of Cd (II).

regulates the rate at which the response probe moves across the electrode surface. EIS plots of the produced electrodes were performed in solution at a voltage of 0 V vs Ag/AgCl throughout a frequency range of 0.1-100000 Hz and an amplitude of 0.005 V for this study's electrochemical impedance spectroscopy (EIS) investigations. Figure 6 shows that the charge transfer resistance value of the HDPBACPE is much higher than that of the unmodified CPE ($R_{ct} = 2053$). In addition, the CdI , R_s , and ZW values were all recorded accurately from the instrument's circuit, whereas these data were all plainly indicative of a successful HDPBA modification of the original, unmodified CPE. The EIS results for $K_3[Fe(CN)_6]$ are in agreement with the CV results, demonstrating that the modifier (HDPBA) was successfully immobilized in the carbon paste electrode and resulting in substantial variations in the surface electrochemical characteristics of the modified and unmodified electrodes. Additionally, EIS spectra were acquired in B-R solution (0.1 M) containing 100 M Cd(II) for both the modified and unmodified electrodes. HDPBA updated EIS plots

CONCLUSION

For the purpose of detecting Cd(II) in a variety of ambient water samples and tobacco samples, a new, simple, highly sensitive, and selective CPE modified with HDPBA has been built in this study. The newly created electrode offers a number of advantages over existing ones. These include a low price, ease of preparation, the ability to be easily renewed, mobility, and a low noise floor. In addition, the proposed electrode displayed a number of intriguing electrochemical behaviors, including superior selectivity, high sensitivity, good stability, rapidity, and the ability to quantify Cd(II) at extremely low concentrations, in comparison to both unmodified CPE and the majority of other reported electrodes. The produced electrode showed excellent repeatability (RSD of 3.8%) and a wide linear range (0.3-100 nM) under optimum experimental conditions. The detection limit was also rather low at 0.032 nM Cd(II). Tobacco and water samples were successfully analyzed for Cd(II) using both the proposed approach and the GFAAS method. Good agreement was discovered between the % recoveries achieved using the two approaches. The proposed approach has been used to determine Cd(II) in tobacco and other water samples, but it may be used for the analysis of Cd(II) in other matrices as well.

REFERENCES

1. S. S. Ghasemi, M. Hadavifar, B. Maleki, and E. Mohammadnia, "Adsorption of mercury ions from synthetic aqueous solution using polydopamine decorated SWCNTs," *Journal of Water Process Engineering*, vol. 32, 2019.
2. M. Baghayeri, A. Amiri, and F. Karimabadi, "Magnetic MWCNTs-dendrimer: a potential modifier for electrochemical evaluation of As(III) ions in real water samples," *Journal of Electroanalytical Chemistry*, vol. 888, 2021.
3. B. Maleki, M. Baghayeri, M. Ghanei-Motlagh et al., "Polyamidoaminedendrimer functionalized iron oxide nanoparticles for simultaneous electrochemical detection of Pb^{2+} and Cd^{2+} ions in environmental waters," *Measurement*, vol. 140, pp. 81–88, 2019.

4. G. Fan, D. Zhai, and D. Zou, "Highly sensitive electrochemical determination of cadmium(II) in environmental water based on the electrodeposited bismuth nanoparticles," *International Journal of Electrochemical Science*, vol. 11, no. 6, pp. 4362–4370, 2016.
5. N. M. *anh, N. D. Luyen, T. *anh Tam Toan, N. Hai Phong, and N. Van Hop, "Voltammetry determination of Pb(II), Cd(II), and Zn(II) at bismuth film electrode combined with 8-hydroxyquinoline as a complexing agent," *Journal of Analytical Methods in Chemistry*, vol. 2019, Article ID 4593135, 11 pages, 2019.
6. X. Wen, P. Wu, L. Chen, and X. Hou, "Determination of cadmium in rice and water by tungsten coil electrothermal vaporization-atomic fluorescence spectrometry and tungsten coil electrothermal atomic absorption spectrometry after cloud point extraction," *Analytica Chimica Acta*, vol. 650, no. 1, pp. 33–38, 2009.
7. A. A. Shaltout, J. Boman, B. Welz, I. N. B. Castilho, E. A. Al Ashkar, and S. M. Gaita, "Method development for the determination of Cd, Cu, Ni and Pb in PM2.5 particles sampled in industrial and urban areas of Greater Cairo, Egypt, using high-resolution continuum source graphite furnace atomic absorption spectrometry," *Microchemical Journal*, vol. 113, no. 2, pp. 4–9, 2014.
8. R. P. Lamsal and D. Beauchemin, "Estimation of the bioaccessible fraction of Cr, As, Cd and Pb in locally available bread using on-line continuous leaching method coupled to inductively coupled plasma mass spectrometry," *Analytica Chimica Acta*, vol. 867, pp. 9–17, 2015.
9. Q. X. Zhou, M. Lei, Y. L. Liu, Y. L. Wu, and Y. Y. Yuan, "Simultaneous determination of cadmium, lead and mercury ions at trace level by magnetic solid phase extraction with Fe@Ag@dimercaptobenzene coupled to high performance liquid chromatography," *Talanta*, vol. 175, pp. 194–199, 2017.
10. F. Xia, X. Zhang, C. Zhou, D. Sun, Y. Dong, and Z. Liu, "Simultaneous determination of copper, lead, and cadmium at ionic liquid immobilized quercetin modified carbon paste electrode," *Journal of Automated Methods & Management in Chemistry*, vol. 2010, Article ID 824197, 6 pages, 2010.
11. C. Kilbride, J. Poole, and T. R. Hutchings, "A comparison of Cu, Pb, As, Cd, Zn, Fe, Ni and Mn determined by acid extraction/ICP-OES and ex situ field portable X-ray fluorescence analyses," *Environmental Pollution*, vol. 143, no. 1, pp. 16–23, 2006.
12. D. Martin-Yerga, M. B. Gonzalez-Garcia, and A. CostaGarcia, "Electrochemical determination of mercury: a review," *Talanta*, vol. 116, pp. 1091–1104, 2013.
13. F. Wang, J. Liu, Y. J. Wu, Y. M. Gao, and X. F. Huang, "Anodic stripping voltammetric determination of mercury (II) in water using a 4-tert-butyl-1-(Ethoxycarbonylmethoxy)*iacalix[4]Arene modified glassy carbon electrode," *Journal of the Chinese Chemical Society*, vol. 56, no. 4, pp. 778–784, 2009.
14. H. Khani, M. K. Rofouei, P. Arab, V. K. Gupta, and Z. Vafaei, "Multi-walled carbon nanotubes-ionic liquid-carbon paste electrode as a super selectivity sensor: application to potentiometric monitoring of mercury ion(II)," *Journal of Hazardous Materials*, vol. 183, no. 1–3, pp. 402–409, 2010.
15. S. E. Hashemi, M. Payehghadr, Z. Eshaghi, and H. Kargar, "Ultra trace level square wave anodic stripping voltammetric sensing of mercury(II) ions in environmental samples using a Schiff base-modified carbon paste electrode," *International Journal of Environmental Analytical Chemistry*, vol. 99, no. 12, pp. 1148–1163, 2019.