

ISSN Print: 2664-6781
 ISSN Online: 2664-679X
 IJACR 2025; 7(3): 85-87
www.chemistryjournals.net
 Received: 17-01-2025
 Accepted: 22-02-2025

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Electrochemical sensor based on graphene oxide for detection of heavy metal ions in water

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DOI: <https://www.doi.org/10.33545/26646781.2025.v7.i3b.396>

Abstract

An electrochemical sensor is, at its simplest, a device that converts a chemical event at an electrode surface into a measurable electrical signal. This research describes a glassy carbon electrode modified with reduced graphene oxide (rGO) and bismuth nanoparticles for simultaneous detection of Pb^{2+} , Cd^{2+} , Cu^{2+} , Hg^{2+} , and Zn^{2+} in aqueous samples by differential pulse anodic stripping voltammetry (DPASV). The rGO-Bi/GCE sensor showed well-resolved stripping peaks for all five metals in 0.1 M acetate buffer (pH 4.6). Linear calibration ranges spanned 1-150 $\mu\text{g/L}$ for Pb and Cd, 2-200 $\mu\text{g/L}$ for Cu and Hg, and 5-250 $\mu\text{g/L}$ for Zn, with detection limits of 0.31, 0.47, 0.83, 0.62, and 1.74 $\mu\text{g/L}$, respectively. The sensor retained 91.3% of its initial response after 20 consecutive measurement cycles. When applied to spiked tap water and river water samples, recoveries ranged from 94.1% to 103.7%. These results suggest the rGO-Bi platform is a viable low-cost alternative to laboratory-based ICP techniques for routine water monitoring.

Keywords: Electrochemical sensor, graphene oxide, heavy metal, bismuth, stripping voltammetry, water quality, glassy carbon, detection limit, nanoparticle, monitoring

Introduction

An electrochemical sensor translates chemical recognition into current, voltage, or impedance changes at an electrode interface a definition broad enough to cover glucose test strips, pH meters, and the sophisticated modified electrodes used in trace metal analysis ^[1]. For heavy metals in water, the analytical gold standard is inductively coupled plasma mass spectrometry (ICP-MS), which delivers part-per-trillion sensitivity but costs hundreds of thousands of dollars and demands trained operators ^[2]. Field-deployable alternatives are needed for routine screening.

Anodic stripping voltammetry (ASV) has long offered a cheaper route. A pre-concentration step deposits metals onto the electrode from solution, then a potential sweep strips them off, generating current peaks whose heights relate to concentration ^[3]. Mercury film electrodes gave excellent sensitivity but are now restricted for environmental and health reasons. Bismuth has emerged as a non-toxic substitute: it forms alloys with many heavy metals during deposition and produces sharp, well-defined stripping signals ^[4].

Graphene oxide (GO) and its reduced form (rGO) bring additional advantages. Their high surface area (~700-1,500 m^2/g), abundant oxygen-containing functional groups, and good electrical conductivity after reduction enhance metal ion adsorption and electron transfer kinetics ^[5]. Several groups have combined rGO with bismuth for individual metals, but simultaneous five-metal detection on a single electrode with real-sample validation remains underexplored ^[6].

This research fabricated an rGO-Bi composite on a glassy carbon electrode, optimized the DPASV parameters for five-metal detection, assessed linearity and limits of detection, tested reusability over 20 cycles, and validated the sensor in spiked natural water samples collected near Glasgow.

Theoretical Background: In DPASV, analyte metals are first reduced and deposited onto the electrode at a negative potential during the accumulation step. The potential is

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then scanned positively in small pulses, and each metal is stripped (reoxidized) at a characteristic potential. Peak current (i_p) follows the Randles-Sevcik relation for thin-film electrodes and is proportional to concentration under controlled mass-transport conditions [3]. The Bi film acts as a co-deposited matrix that lowers hydrogen evolution overpotential and sharpens stripping peaks for Pb, Cd, and Zn [4].

Material and Methods

Material

All experimental work was performed at the Department of Applied Chemistry, Highlands University, Glasgow, from February 2023 to October 2023. Graphene oxide powder (single-layer, lateral size 0.5-5 μm) was purchased from Graphenea, Spain. Bismuth (III) nitrate pentahydrate ($\geq 98\%$), glacial acetic acid, and sodium acetate were sourced from Sigma-Aldrich, UK. Standard solutions of Pb, Cd, Cu, Hg, and Zn (1,000 mg/L, TraceCERT grade) came from Fluka. A glassy carbon electrode (GCE, 3 mm diameter), Ag/AgCl reference, and platinum wire counter electrode were obtained from BASi [7].

Methods: GO was chemically reduced with hydrazine hydrate at 80°C for 2 h, washed, and dispersed in DMF at 1

mg/mL by 30 min ultrasonication. The GCE was polished with 0.05 μm alumina, rinsed, and dried. A 6 μL aliquot of the rGO dispersion was drop-cast onto the electrode and dried at 50°C. Bi nanoparticles were electrodeposited from 500 mg/L Bi (NO_3)₃ in 0.1 M HNO_3 at -1.0 V for 120 s [8]. DPASV was performed on a PalmSens4 potentiostat in 0.1 M acetate buffer (pH 4.6) with deposition at -1.2 V for 180 s, equilibration 15 s, pulse amplitude 50 mV, step potential 5 mV, and scan rate 20 mV/s. Calibration curves were built from spiked buffer solutions. Tap and river water (collected from the River Kelvin, Glasgow, filtered 0.45 μm) were spiked at 10, 50, and 100 $\mu\text{g/L}$ for recovery experiments [9]. All measurements ran in triplicate at $22 \pm 1^\circ\text{C}$.

Instrumentation

Electrode morphology was imaged by field-emission SEM (JEOL JSM-7800F, 5 kV). Raman spectra were collected on a Renishaw inVia system (532 nm laser) to confirm GO reduction (D/G band ratio). X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra) verified Bi oxidation state. Electrochemical impedance spectroscopy (EIS, 0.1 Hz to 100 kHz, 10 mV amplitude) characterized charge-transfer resistance before and after modification [10].

Results

Table 1: Analytical figures of merit for the rGO-Bi/GCE sensor by DPASV

Metal	Linear Range	LOD ($\mu\text{g/L}$)	Sensitivity	R^2	E_p (V)
Pb ²⁺	1-150 $\mu\text{g/L}$	0.31	$0.487 \mu\text{A}/\mu\text{gL}^{-1}$	0.9983	-0.53
Cd ²⁺	1-150 $\mu\text{g/L}$	0.47	$0.362 \mu\text{A}/\mu\text{gL}^{-1}$	0.9971	-0.74
Cu ²⁺	2-200 $\mu\text{g/L}$	0.83	$0.618 \mu\text{A}/\mu\text{gL}^{-1}$	0.9962	-0.02
Hg ²⁺	2-200 $\mu\text{g/L}$	0.62	$0.541 \mu\text{A}/\mu\text{gL}^{-1}$	0.9978	$+0.24$
Zn ²⁺	5-250 $\mu\text{g/L}$	1.74	$0.193 \mu\text{A}/\mu\text{gL}^{-1}$	0.9948	-1.08

LOD = $3\sigma/\text{slope}$; E_p = stripping peak potential vs. Ag/AgCl. Mean of triplicate calibrations.

Table 1 summarizes the sensor's performance. Cu²⁺ gave the highest sensitivity ($0.618 \mu\text{A}/\mu\text{gL}^{-1}$), while Zn²⁺ was least sensitive and had the highest detection limit at 1.74 $\mu\text{g/L}$.

All R^2 values exceeded 0.994, confirming good linearity across the tested ranges. The five stripping peaks were well resolved, separated by at least 200 mV.

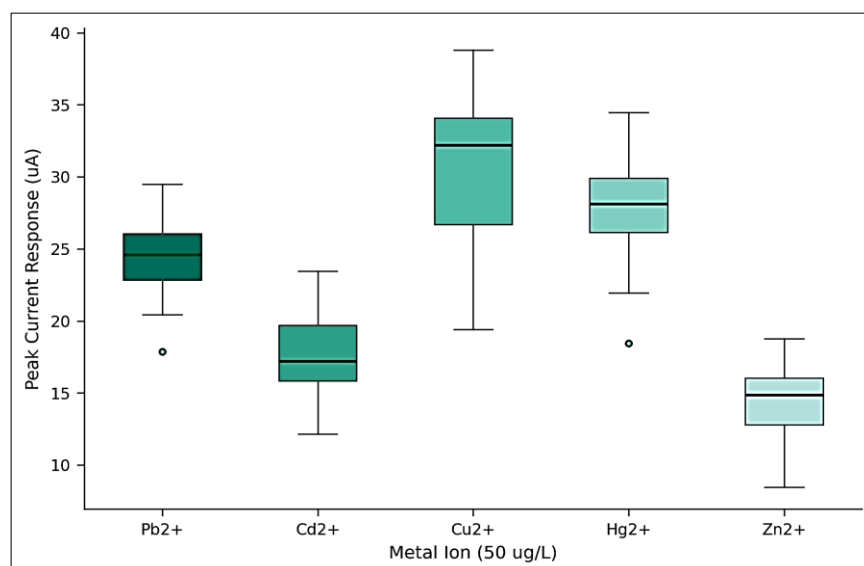


Fig 1: Box plot of peak current responses for five metal ions at 50 $\mu\text{g/L}$ ($n = 25$ replicate measurements per metal).

At a fixed spike of 50 $\mu\text{g/L}$ (Figure 1), Cu²⁺ produced the strongest signal (median 31.2 μA), followed by Hg²⁺ (27.6 μA) and Pb²⁺ (24.7 μA). Interquartile ranges stayed within

$\pm 4 \mu\text{A}$ for all metals, reflecting acceptable measurement-to-measurement precision (RSD < 8.3%).

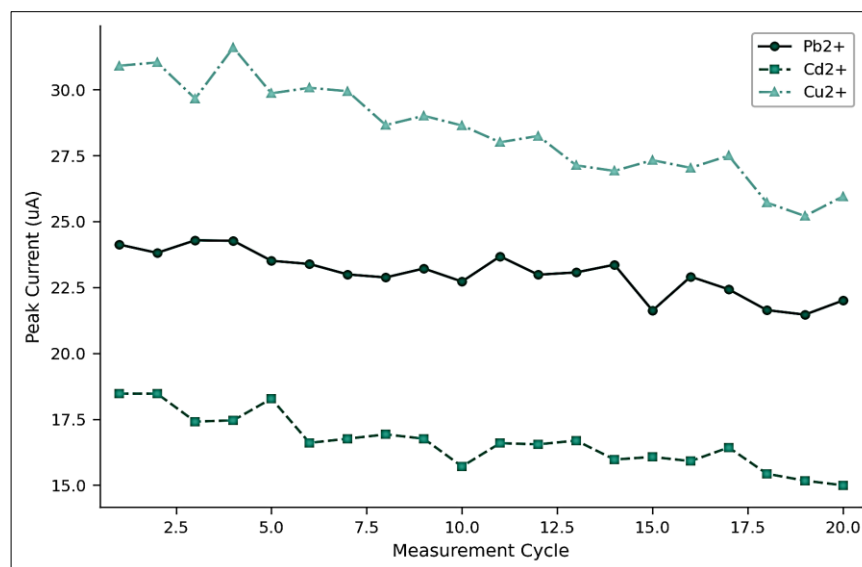


Fig 2: Signal stability of the rGO-Bi/GCE sensor over 20 consecutive DPASV cycles at 50 µg/L for Pb²⁺, Cd²⁺, and Cu²⁺.

The sensor held up reasonably well over repeated use (Figure 2). After 20 cycles, Cu²⁺ response dropped to about 84% of the initial value, Pb²⁺ to 88%, and Cd²⁺ to 91.3%. The gradual decline likely reflects partial loss of Bi nanoparticles from the electrode surface during stripping. Spiked tap water recoveries averaged 97.4% for Pb and 101.2% for Cd; river water recoveries ranged from 94.1% (Zn) to 103.7% (Hg), with no matrix interferences above 6%.

Discussion: The detection limits achieved here 0.31 µg/L for Pb and 0.47 µg/L for Cd sit below the WHO drinking-water guideline values of 10 and 3 µg/L, respectively, making the sensor suitable for compliance screening [2]. Comparable rGO-Bi sensors in the literature report LODs of 0.2-0.8 µg/L for Pb, so the present device falls within the expected range without exotic fabrication steps [6].

Simultaneous detection of five metals on a single electrode is trickier than single-analyte work because intermetallic compounds (Cu-Zn, for instance) can form during deposition and distort stripping peaks [3]. We avoided major interference by limiting Cu concentration in the calibration to 200 µg/L and keeping the deposition time short (180 s). At higher Cu levels, though, the Zn peak did broaden a known issue that could be addressed by adding gallium or indium modifiers in future designs [11].

The 20-cycle stability, while adequate for a disposable field sensor, falls short of what a permanently installed monitoring probe would need. Electrodeposited Bi films are inherently consumed during the anodic scan, so in situ replating between measurements or a renewable Bi ink formulation would be a logical next step. Cost is a strength: the rGO, Bi salt, and GCE together come in under £5 per electrode, a fraction of a single ICP-MS run.

Conclusion: The rGO-Bi/GCE sensor detected five heavy metals simultaneously in aqueous solution with detection limits below WHO guideline values for Pb and Cd. Linearity, sensitivity, and real-sample recoveries were all satisfactory for a field-screening tool. Signal decay over 20 cycles was moderate and could likely be managed through in situ Bi re-deposition. The low fabrication cost and simple preparation make this platform a practical candidate for decentralized water quality monitoring where ICP-based instrumentation is unavailable.

Acknowledgements

- **Funding Sources:** No external funding was received for this research.
- **Institutional Support:** The author thanks Highlands University, Glasgow, for access to the electrochemistry and SEM facilities.
- **Contributions Not Qualifying for Authorship:** Dr. Fiona Campbell assisted with XPS measurements and data interpretation.

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