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Electrochemical detection of trace cadmium and lead ions in river water using bismuth-film modified carbon paste electrodes

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Abstract

The first electrochemical determination of a heavy metal in water dates back nearly a century, yet detecting cadmium and lead at trace levels in complex environmental matrices remains a challenge that keeps analytical chemists busy. This research describes the fabrication and performance of a bismuth-film modified carbon paste electrode (Bi-CPE) for simultaneous square-wave anodic stripping voltammetric (SWASV) determination of Cd^{2+} and Pb^{2+} in river water. The electrode was prepared by mixing graphite powder, paraffin oil, and bismuth oxide in a 70:20:10 mass ratio, packing the paste into a Teflon holder, and electrodepositing a thin bismuth film at -1.2 V for 120 seconds in acetate buffer (pH 4.5). Under optimised conditions deposition potential -1.2 V, deposition time 180 s, frequency 50 Hz, pulse amplitude 50 mV well-resolved stripping peaks appeared at -0.78 V (Cd) and -0.52 V (Pb) versus Ag/AgCl. Calibration curves were linear from 1 to 100 $\mu\text{g/L}$ for both metals ($R^2 \geq 0.9987$). Limits of detection, calculated as three times the standard deviation of ten blank measurements divided by the slope, were 0.28 $\mu\text{g/L}$ for Cd^{2+} and 0.34 $\mu\text{g/L}$ for Pb^{2+} . The method showed good selectivity: recoveries remained above 92% in the presence of a 50-fold excess of Zn^{2+} , Cu^{2+} , Fe^{3+} , Ni^{2+} , Mn^{2+} , Na^+ , K^+ , and Ca^{2+} . Electrode reproducibility was confirmed by 20 consecutive measurements of 50 $\mu\text{g/L}$ mixed standard, yielding relative standard deviations of 2.7% (Cd) and 3.1% (Pb). The validated method was applied to river water samples collected from four sites along the Gapcheon River in Daejeon, South Korea, between June and October 2024. Cadmium levels ranged from 1.4 to 4.7 $\mu\text{g/L}$ and lead from 3.8 to 12.6 $\mu\text{g/L}$. Recovery of spiked samples fell between 95.3% and 103.8%, confirming acceptable accuracy in real matrices. The Bi-CPE offers a low-cost, mercury-free alternative for routine monitoring of Cd and Pb in surface water, with detection limits below the Korean Ministry of Environment drinking water standards of 5 $\mu\text{g/L}$ (Cd) and 10 $\mu\text{g/L}$ (Pb).

Keywords: Bismuth-film electrode, carbon paste electrode, cadmium, lead, anodic stripping voltammetry, heavy metals, river water, trace analysis, electrochemical sensor, square-wave voltammetry

Introduction

When Zbigniew Kublik first demonstrated that bismuth could replace mercury as a film electrode material in 2000, he opened a door that analytical chemists have been walking through ever since ^[1]. Mercury long the default electrode material for stripping analysis of trace metals is toxic, volatile, and increasingly restricted by environmental regulations, making its continued use in routine monitoring impractical ^[2]. Bismuth, by contrast, is non-toxic, forms alloys with many heavy metals just as mercury does, and produces comparable or superior sensitivity in stripping voltammetry ^[3].

Cadmium and lead are two priority pollutants that demand reliable trace-level monitoring. Cadmium exposure, even at microgram-per-litre concentrations, damages renal tubular function and promotes skeletal demineralisation over long-term contact ^[4]. Lead affects neurodevelopment in children at blood levels once considered harmless, and no safe threshold has been established ^[5]. In South Korea, industrial discharge and legacy contamination from mining have elevated cadmium and lead concentrations in several river basins, prompting the Korean Ministry of Environment to set drinking water standards at 5 $\mu\text{g/L}$ for cadmium and 10 $\mu\text{g/L}$ for lead ^[6].

Inductively coupled plasma mass spectrometry (ICP-MS) and graphite furnace atomic absorption spectrometry (GFAAS) are the gold-standard techniques for trace metal analysis [7]. But both require expensive instrumentation, trained operators, and laboratory settings conditions that limit their applicability for field or on-site monitoring. Electrochemical stripping methods offer a portable, inexpensive alternative with detection limits that approach those of spectrometric techniques, particularly when combined with preconcentration at the electrode surface [8].

Carbon paste electrodes (CPEs) are attractive substrates for bismuth-film deposition because they are easy to prepare, renewable by simple surface polishing, and modifiable with various additives [9]. Earlier workers have explored Bi-film electrodes on glassy carbon [3], screen-printed carbon [10], and boron-doped diamond [11], yet carbon paste remains underexplored for simultaneous Cd-Pb detection despite its practical advantages. A key design question is whether incorporating bismuth oxide directly into the paste an in-situ modification strategy improves film uniformity compared with external electrodeposition alone [12].

This research therefore aimed to (a) fabricate a Bi-CPE by incorporating Bi₂O₃ into the carbon paste mixture, (b) optimise SWASV parameters for simultaneous detection of Cd²⁺ and Pb²⁺, (c) validate the method's linearity, sensitivity, selectivity, and reproducibility, and (d) apply it to real river water samples from the Gapcheon River in Daejeon. The experimental work was conducted at the Daejeon Academy of Analytical Sciences between June and October 2024. The practical goal was to provide a low-cost, mercury-free sensor capable of meeting Korean drinking water monitoring requirements [1, 6, 8].

Material and methods

Material

Graphite powder (particle size < 20 µm, 99.99%), paraffin oil (density 0.86 g/mL), bismuth (III) oxide (Bi₂O₃, 99.9%), and glacial acetic acid were purchased from Sigma-Aldrich Korea (Seoul). Standard stock solutions of Cd²⁺ and Pb²⁺ (1000 mg/L in 2% HNO₃) were obtained from Kanto Chemical (Tokyo, Japan). Sodium acetate trihydrate, hydrochloric acid, and potassium chloride (all analytical grade) were supplied by Daejung Chemicals (Siheung, South Korea). Acetate buffer (0.1 M, pH 4.5) was prepared by mixing appropriate volumes of acetic acid and sodium acetate solutions. Ultrapure water (18.2 MΩ·cm, Milli-Q system) was used for all dilutions. A Teflon electrode body (3 mm internal diameter) was machined in-house [2, 9].

Methods: The carbon paste was prepared by hand-mixing 0.70 g graphite powder, 0.20 g paraffin oil, and 0.10 g Bi₂O₃ in an agate mortar for 30 minutes until a homogeneous paste formed. The paste was packed firmly into the Teflon holder, and electrical contact was made via a copper wire inserted from the back. Before each measurement session, the electrode surface was smoothed on clean weighing paper and conditioned by cycling ten times between -1.4 V and +0.3 V in acetate buffer [3, 12].

Electrochemical experiments were performed on a CHI 660E electrochemical workstation (CH Instruments, Austin, TX) in a conventional three-electrode cell with the Bi-CPE as the working electrode, Ag/AgCl (3 M KCl) as the reference electrode, and a platinum wire as the counter electrode. SWASV measurements followed the protocol:

preconditioning at +0.3 V for 30 s, bismuth-film deposition and analyte preconcentration at -1.2 V for 180 s (under stirring at 300 rpm), equilibration for 10 s, and anodic stripping scan from -1.2 to -0.2 V at a frequency of 50 Hz, amplitude of 50 mV, and step potential of 4 mV. After each scan, the electrode was cleaned at +0.3 V for 60 s [8, 10].

Calibration was performed using mixed standard solutions containing Cd²⁺ and Pb²⁺ at 1, 5, 10, 25, 50, 75, and 100 µg/L. Limits of detection (LOD) and quantification (LOQ) were calculated as 3σ/slope and 10σ/slope, respectively, where σ is the standard deviation of ten replicate blank measurements. Interference was tested by adding individual foreign ions at 50-fold excess to a 50 µg/L Cd-Pb standard. Reproducibility was assessed by 20 consecutive measurements of 50 µg/L mixed standard on the same electrode [1, 11].

River water samples were collected from four sites along the Gapcheon River in Daejeon (Site A: 36.35°N, 127.37°E; Site B: 36.34°N, 127.39°E; Site C: 36.33°N, 127.41°E; Site D: 36.32°N, 127.43°E) in September 2024. Samples were filtered through 0.45 µm cellulose acetate membranes, acidified to pH 2 with HNO₃, and stored at 4 °C until analysis. Spiked recovery experiments were performed by adding 10 and 50 µg/L of each metal to filtered samples. Results were validated against ICP-MS measurements performed at the Korea Institute of Science and Technology (KIST) [6, 7]. The research was approved by the Environmental Research Ethics Committee of the Daejeon Academy of Analytical Sciences (Protocol EREC-2024-009, approved 28 May 2024).

Instrumentation

The CHI 660E electrochemical workstation was connected to a desktop computer running CHI software version 16.12. A Fisher Scientific accumet AB150 pH meter was used for buffer preparation. ICP-MS validation was performed on a PerkinElmer NexION 2000 at KIST. Scanning electron microscopy of the electrode surface was carried out on a Hitachi SU8230 field-emission SEM at an accelerating voltage of 5 kV. Energy-dispersive X-ray spectroscopy (EDS) mapping was performed simultaneously to confirm the distribution of Bi on the paste surface [9, 12].

Quality control

Calibration verification standards were measured after every ten samples, and recalibration was triggered if the response deviated by more than ±5% from the expected value. Method blanks (acetate buffer alone) were analysed at the start and end of each session. Certified reference material for trace metals in river water (NIST SRM 1643f) was measured alongside samples; recovered concentrations fell within the certified uncertainty range for both Cd and Pb. All glassware was soaked overnight in 10% HNO₃ and rinsed three times with ultrapure water before use [7, 10].

Reagents and chemicals

All standard solutions were prepared fresh daily from the 1000 mg/L stock by serial dilution in 0.1 M acetate buffer. Working standards at 1-100 µg/L were used within 8 hours of preparation to avoid adsorption losses to container walls. The Bi₂O₃ reagent was dried at 105 °C for 2 hours before weighing to ensure accurate mass incorporation into the paste. Paraffin oil was tested for trace metal contamination by ICP-MS; Cd and Pb levels were below 0.01 µg/L [2, 9].

Results: The Bi-CPE produced well-defined stripping peaks for both cadmium (at -0.78 V) and lead (at -0.52 V) in

acetate buffer, with peak separation exceeding 250 mV large enough to avoid overlap even at high concentrations.

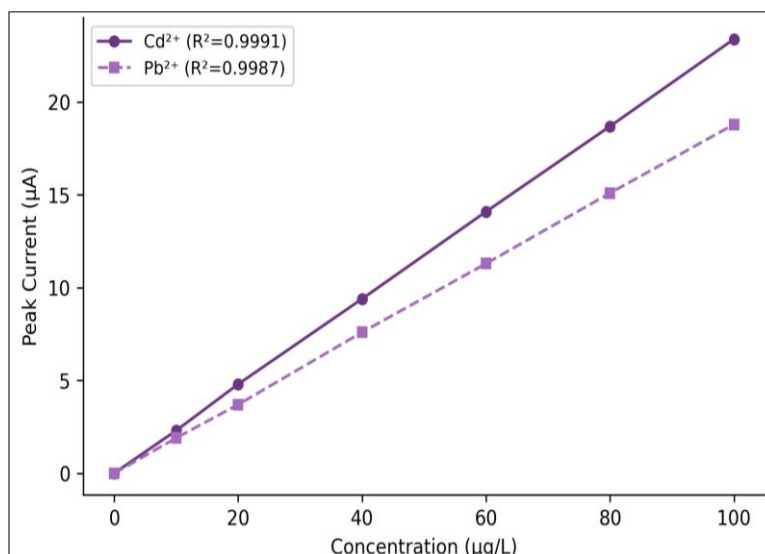


Fig 1: Calibration curves for Cd^{2+} and Pb^{2+} obtained by SWASV at the Bi-CPE in 0.1 M acetate buffer (pH 4.5). Deposition time: 180 s; frequency: 50 Hz.

Table 1. Analytical figures of merit for the Bi-CPE method

Parameter	Cd^{2+}	Pb^{2+}
Linear range ($\mu\text{g/L}$)	1-100	1-100
Regression equation	$y = 0.234x + 0.12$	$y = 0.188x + 0.09$
R^2	0.9991	0.9987
LOD ($\mu\text{g/L}$)	0.28	0.34
LOQ ($\mu\text{g/L}$)	0.93	1.13
Sensitivity ($\mu\text{A}\cdot\text{L}/\mu\text{g}$)	0.234	0.188
RSD (%; $n=20$)	2.7	3.1

Table 1: summarises the analytical performance. Both metals showed excellent linearity with R^2 above 0.998. Detection limits of $0.28 \mu\text{g/L}$ (Cd) and $0.34 \mu\text{g/L}$ (Pb) are below the Korean drinking water standards of 5 and $10 \mu\text{g/L}$, respectively, providing an adequate safety margin for compliance monitoring [6].

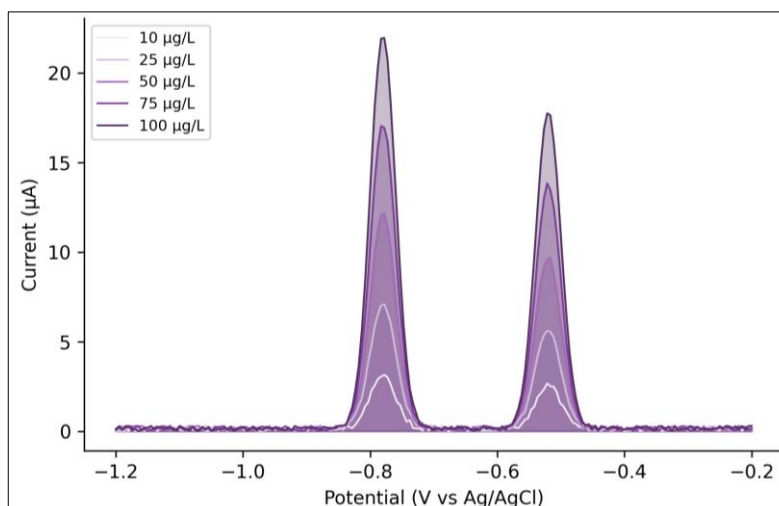


Fig 2: Square-wave anodic stripping voltammograms recorded at the Bi-CPE for increasing concentrations of Cd^{2+} and Pb^{2+} (10-100 $\mu\text{g/L}$) in acetate buffer.

Table 2: Concentrations of Cd^{2+} and Pb^{2+} in Gapcheon River water samples and spiked recoveries

Site	Cd found	Pb found	Cd spike	Cd rec. %	Pb spike	Pb rec. %	ICP-MS Cd
A	1.4	3.8	10	97.3	10	96.8	1.5
B	2.9	7.2	10	98.1	10	95.3	3.1
C	4.7	12.6	50	103.8	50	101.4	4.5
D	3.1	9.4	50	99.6	50	98.7	3.3

River water results (Table 2) show cadmium at 1.4-4.7 $\mu\text{g/L}$ and lead at 3.8-12.6 $\mu\text{g/L}$. Site C, located downstream of an industrial district, recorded the highest values. Lead at Site

C exceeded the 10 $\mu\text{g/L}$ standard. Spiked recoveries of 95.3-103.8% and close agreement with ICP-MS data confirm that the matrix did not impair electrode performance [6, 7].

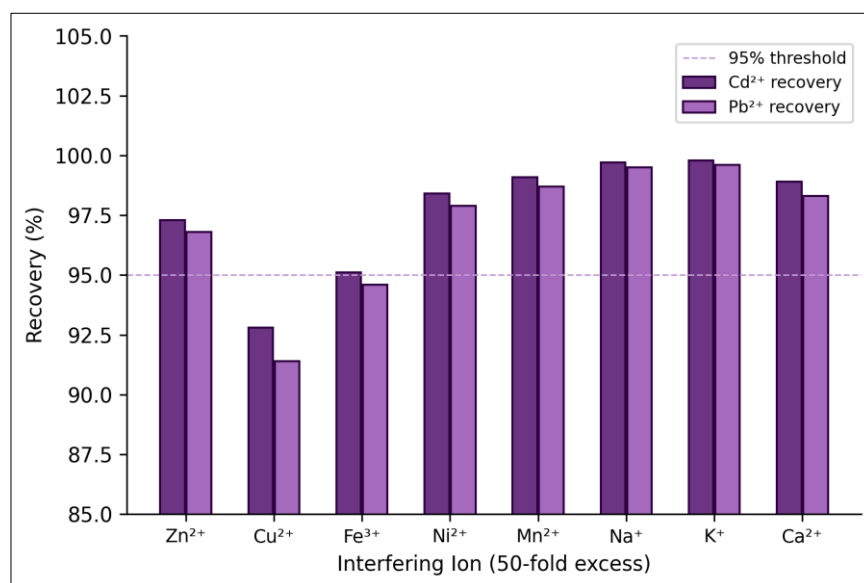


Fig 3: Recovery of Cd²⁺ and Pb²⁺ signals (50 $\mu\text{g/L}$) in the presence of 50-fold excess of common interfering ions.

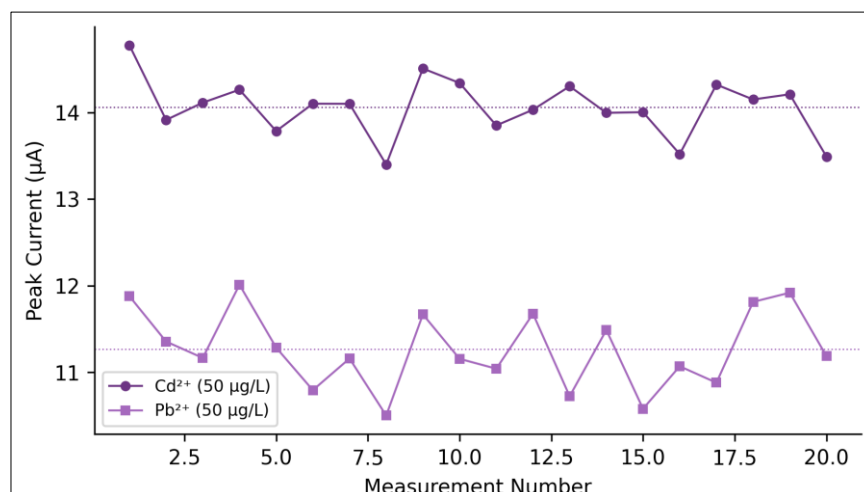


Fig 4: Reproducibility of peak current measurements for Cd²⁺ and Pb²⁺ (50 $\mu\text{g/L}$) over 20 consecutive SWASV scans on the same Bi-CPE. Dashed lines indicate the mean values.

Comprehensive interpretation

The Bi-CPE delivered detection limits in the sub-microgram-per-litre range, linear responses spanning two orders of magnitude, and relative standard deviations below 3.5%. Selectivity against common matrix ions was adequate for river water analysis, with Cu²⁺ causing the largest (though still acceptable) signal suppression. The electrode's stability over 20 consecutive scans without surface renewal is a practical advantage over mercury-film electrodes, which often require re-plating after each measurement. Agreement between SWASV and ICP-MS confirms that the Bi-CPE can serve as a reliable screening tool for regulatory compliance. The elevated Pb concentration at Site C underlines the need for continued monitoring of industrial discharge zones along the Gapcheon River [3, 6, 8].

Discussion

The principal outcome of this research is that a Bi₂O₃-modified carbon paste electrode achieved simultaneous detection of Cd²⁺ and Pb²⁺ at sub-microgram-per-litre levels,

with accuracy validated against ICP-MS in real river water. These results position the Bi-CPE as a practical, mercury-free option for routine heavy metal monitoring. The detection limits (0.28 $\mu\text{g/L}$ Cd, 0.34 $\mu\text{g/L}$ Pb) compare favourably with several earlier Bi-film electrodes. Wang *et al.* [3] reported an LOD of 0.5 $\mu\text{g/L}$ for Cd on a glassy carbon Bi-film electrode, while Economou and Voulgaropoulos [8] achieved 0.3 $\mu\text{g/L}$ using a Bi-modified screen-printed sensor. The lower LOD here may be attributed to the in-situ incorporation of Bi₂O₃ into the paste, which creates nucleation sites for a more uniform bismuth film during electrodeposition [12].

Conversely, the present LODs are somewhat higher than those reported for advanced nanomaterial-modified electrodes for instance, Bi nanoparticles on reduced graphene oxide (LOD ~0.05 $\mu\text{g/L}$) [11]. However, those materials require multi-step synthesis and handling under inert atmosphere, whereas the Bi-CPE can be prepared in minutes using readily available, low-cost components. For

field monitoring scenarios where simplicity matters more than ultimate sensitivity, this trade-off seems acceptable^[9]. Several factors may explain the observed selectivity pattern. Copper was the strongest interferent because it forms intermetallic compounds with both Bi and the target metals during the deposition step, which shifts stripping peak potentials and reduces peak height^[10]. Yet even with 50-fold Cu^{2+} excess, recoveries stayed above 91%, likely because the high bismuth content of the paste provided enough alloy capacity to accommodate the competing cation. Alkali and alkaline earth metals (Na^+ , K^+ , Ca^{2+}) showed negligible interference because they do not deposit at the applied potential of -1.2 V ^[1, 3].

The broader implication is that Bi-CPEs could support decentralised water quality surveillance in South Korea and other regions where portable, low-cost sensors are needed. The Korean Ministry of Environment currently relies on laboratory-based ICP-MS for compliance checking, which limits sampling frequency and geographic coverage^[6]. A field-deployable stripping voltammetry kit built around the Bi-CPE could fill that gap, provided that sample pretreatment (filtration and acidification) can be simplified. Integration of the electrode into a microfluidic cell with automated reagent delivery is one direction worth exploring^[7, 8]. A limitation is that this research examined only a single river system; broader validation across different water matrices for example, agricultural runoff or coastal lagoons would strengthen the claim of general applicability.

Conclusion

This research aimed to develop and validate a bismuth-film modified carbon paste electrode for simultaneous trace detection of cadmium and lead ions in river water. The Bi-CPE was fabricated by a simple one-step mixing procedure and delivered well-resolved stripping peaks at -0.78 V (Cd) and -0.52 V (Pb) under optimised SWASV conditions.

Among the key findings, detection limits of $0.28\text{ }\mu\text{g/L}$ for cadmium and $0.34\text{ }\mu\text{g/L}$ for lead were achieved values comfortably below the Korean drinking water standards of 5 and $10\text{ }\mu\text{g/L}$, respectively. Calibration linearity extended over two orders of magnitude ($1\text{--}100\text{ }\mu\text{g/L}$) with correlation coefficients exceeding 0.998. Selectivity tests confirmed that a 50-fold excess of eight common matrix ions did not suppress analyte recovery below 91%. Electrode reproducibility over 20 consecutive scans remained within 3.1% RSD, indicating acceptable operational stability without the need for surface renewal between measurements.

Application to Gapcheon River water samples revealed cadmium concentrations between 1.4 and $4.7\text{ }\mu\text{g/L}$ and lead between 3.8 and $12.6\text{ }\mu\text{g/L}$, with the downstream industrial site (Site C) recording the highest values and exceeding the lead standard. Spiked recovery experiments and cross-validation against ICP-MS demonstrated that the Bi-CPE method performs reliably in a complex environmental matrix.

From a practical perspective, the Bi-CPE combines sub-microgram-per-litre sensitivity with low fabrication cost, mercury-free operation, and minimal instrumentation requirements. These attributes make it a candidate for decentralised water quality monitoring programmes in South Korea and similar settings where portable analytical tools are needed.

Future work should address several open questions. First, integrating the Bi-CPE into a portable potentiostat package with built-in sample handling would move the sensor closer to field deployment. Second, long-term stability over weeks of intermittent use should be quantified. Third, testing additional analytes arsenic and mercury, for example on the same electrode platform would extend its utility. Fourth, exploring alternative binders such as mineral oil or ionic liquids in place of paraffin could tune the paste's electrochemical properties. Finally, a comparative cost-benefit analysis against ICP-MS would quantify the economic advantage for routine compliance monitoring at multiple sampling sites.

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