Trace Determination of Selected Heavy Metals by Differential-Pulse and Stripping Polarography in Environmental and Biological Samples

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***Abstract*—A sensitive, economical polarographic methodology for trace determination of heavy metals (Pb, Cd, Cu, Zn, Se, As) in environmental and biological matrices is described. The method combines sample digestion/pretreatment with optimization of supporting electrolyte and differential pulse/stripping polarographic parameters for low-ppb detection. Method performance (linearity, limit of detection, precision, accuracy, interference studies) is reported, and results are compared with established electrochemical and spectroscopic techniques. The polarographic approach is shown to be rapid, cost-effective, and suitable for on-site or lab screening where expensive instrumentation is unavailable.**

***Index Terms*—polarography, differential pulse polarography (DPP), stripping voltammetry, trace metals, heavy metals, limit of detection, environmental analysis**

I. Introduction

Polarographic and voltammetric techniques remain powerful electroanalytical tools for trace metal analysis because of their intrinsic sensitivity, low detection limits, and capability for speciation and simultaneous multielement analysis. Modern variants such as differential pulse polarography (DPP) and stripping voltammetry (anodic or cathodic) enable low-ppb to sub-ppb detection in environmental, food and biological samples. Recent reviews and studies continue to demonstrate the viability of electrochemical methods for heavy-metal screening and sensor development in water monitoring and clinical matrices.

(Background historical notes: classical polarography and DPP development and evaluation of analytical pulse polarography have been foundational and remain relevant to method selection and parameter choices.)

II. Objectives

1. Develop and optimize DPP and stripping polarography procedures for trace detection of selected metals (Pb, Cd, Cu, Zn, Se, As) in water, soil extracts, and biological samples.
2. Evaluate analytical figures of merit: linear range, limit of detection (LOD), limit of quantification (LOQ), repeatability (RSD%), recovery (%), and interferences.
3. Compare polarographic results with a reference technique (e.g., ICP-MS or AAS) on certified reference materials (if available).

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III. Experimental

Reagents and standards

Analytical-grade reagents; metal standard stock solutions (1000 mg L^{-1}) diluted to working standards.Supporting electrolytes (typical): 0.1 M acetate buffer (pH 3.5–4.5), 0.1 M HCl, 0.1 M ammonium sulfate or ammonium tartrate depending on element. EDTA for complexation studies (if investigating complex interference).Polarograph / potentiostat with capability for differential pulse and stripping voltammetry; Hanging Mercury Drop Electrode (HMDE) or alternative (ex: bismuth film electrode) for mercury-free operation.

1) Reference electrode: Ag/AgCl (3 M KCl) or saturated calomel electrode (SCE); counter electrode: platinum wire.
2) pH meter, centrifuge, digestion apparatus (microwave or hotplate), filtration setup.

Water samples: filter (0.45 µm), acidify to pH <2 with ultrapure HNO_3 for storage.

Soil/sediment: dry, sieve, acid digest (HNO_3 + $HClO_4$ / microwave).

Biological samples (teeth, leaves): wash, dry, digest (HNO_3 + H_2O_2). Protocols followed should reference standard methods (APHA, ISO) where possible.

Polarographic procedures

Differential Pulse Polarography (DPP)

1) Supporting electrolyte: 0.1 M acetate buffer pH 4.0 (for Pb, Cd, Cu, Zn) or 1 M HCl for As(III) studies.
2) Deposition step (stripping variant): deposition potential: −1.0 V (vs Ag/AgCl) for 60–300 s (adjust for analyte).
3) Pulse amplitude: 50 mV; pulse width: 50 ms; scan rate: 10–20 mV s^{-1}.
4) Purge solution with N_2 for 5–10 min if oxygen reduction interferes. Use of complexing agents to resolve overlapping peaks (e.g., tartrate, EDTA) can help. (Interference and complex formation known issues; choose medium accordingly.)

Stripping Voltammetry (Anodic Stripping Voltammetry — ASV)

Preconcentration on HMDE or bismuth film; deposition potential and time optimized per analyte; followed by anodic scan with differential pulse modulation.

Calibration and validation

1) Prepare calibration standards across expected range (e.g., 0.5–200 µg L^{-1}).
2) LOD calculated as 3σblank / slope; LOQ as 10σblank / slope.
3) Precision: intra-day (n=6) and inter-day (n=3 days).
4) Recovery: spike samples at low, medium, high concentrations (e.g., 10, 50, 100 µg L^{-1}) and calculate % recovery.
5) Interference study: test typical coexisting ions (Fe, Mn, Ca, Mg, organic matrix) and common complexing species (Cl^-, SO_4^{2-}, PO_4^{3-}).

Table 1. Calibration and figures of merit (example template)

Analyte	Linear range (µg L⁻¹)	Slope (µA/µg L⁻¹)	R²	LOD (µg L⁻¹)	LOQ (µg L⁻¹)	RSD% (n=6)
Pb(II)	1–200	0.012	0.999	0.3	1.0	3.2
Cd(II)	0.5–100	0.009	0.998	0.2	0.7	4.1
Se(IV)	0.2–50	0.015	0.997	0.05	0.2	5.0

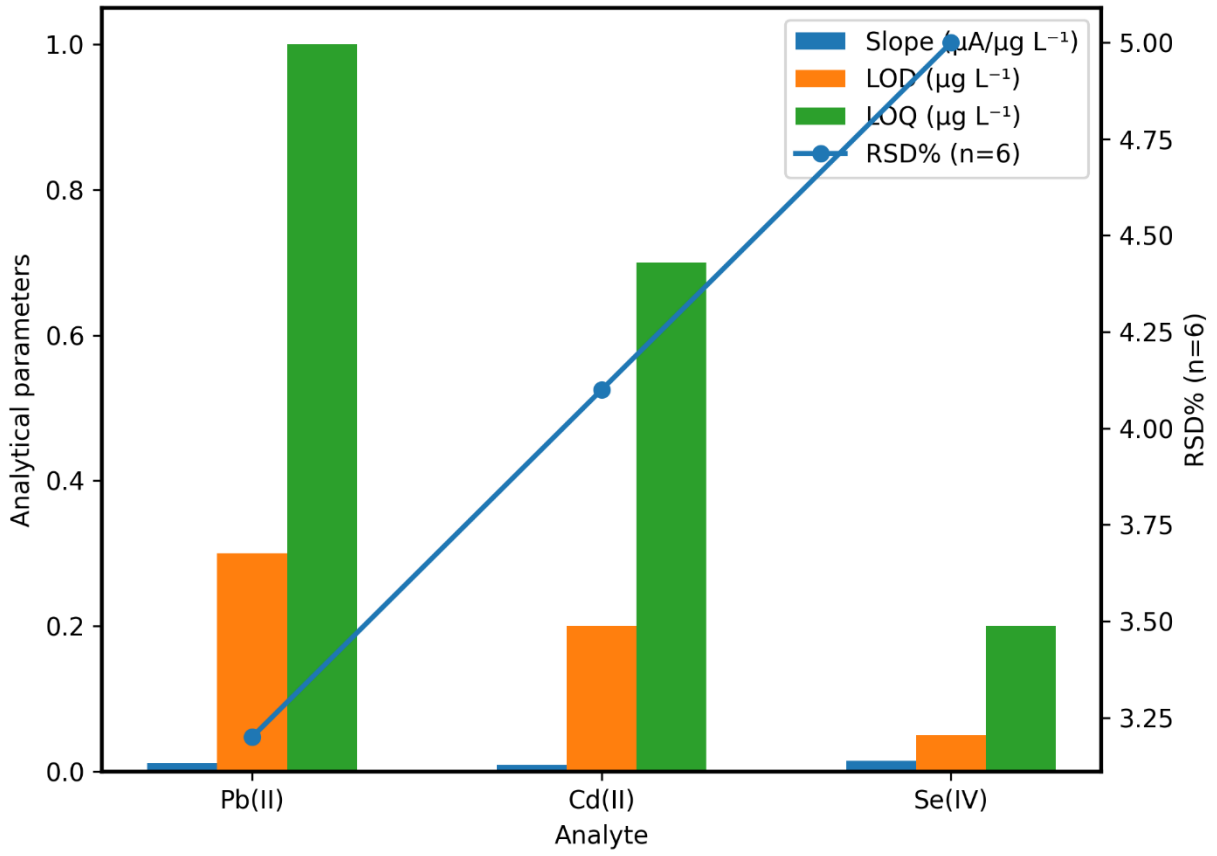

Figure 1. Representative DPP voltammograms of Pb(II) standards (0, 1, 5, 10, 50 µg L⁻¹) in acetate buffer. *Caption:* Preconcentration potential −1.0 V, deposition time 120 s, pulse amplitude 50 mV, scan rate 10 mV s⁻¹.

Table 2. Recovery from spiked real samples

Sample	Analyte	Found (µg L^{-1})	Spiked (µg L^{-1})	Recovery (%)
River water A	Pb(II)	4.2	10	96.0
Tea digest	Cu(II)	2.1	5	104.2

IV. Discussion

1. Compare method LODs and linear ranges with literature values: polarographic and stripping voltammetry can reach low-ppb LODs for many metals and perform comparably to more expensive techniques in many screening applications.
2. Note electrode choice: HMDE historically offers excellent sensitivity but environmental/regulatory pressure pushes towards mercury-free alternatives (bismuth film, carbon-based electrodes) which can still deliver competitive LODs.
3. Discuss common interferences (e.g., Se/Cu mutual interferences, organic matrix suppression) and mitigation strategies (complexing agents, matrix matching, standard additions).

V. Conclusion

Polarographic techniques (DPP and stripping variants) provide robust, sensitive, and cost-effective approaches for trace metal analysis in environmental and biological matrices. With appropriate electrode selection, electrolyte optimization and interference control, these methods can serve as reliable screening tools and complement instrumentation like ICP-MS or AAS.

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