

# Detection of Total Mercury in Water Samples Collected from Sindh using a modified gold electrode coupled with anodic stripping voltammetry

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## Abstract

Mercury (Hg) is recognized as one of the most toxic heavy metals due to its persistence, bioaccumulation, and severe impact on human health and aquatic ecosystems. Even at trace concentrations, exposure to Hg can lead to neurological, renal, and developmental disorders, making its monitoring in environmental samples critically important. Therefore, this study aimed to detect total Hg in fresh and waste water samples by anodic stripping voltammetry using a modified gold electrode. For this purpose, water samples from 5 different regions of Sindh were collected in plastic bottles and transported to the NCEAC Lab. The signal of aqueous Hg(II) was measured in differential pulse anodic Stripping Voltammetry (DPASV) mode, while the effects of deposition potential and deposition time on the analytical signal were examined. The supporting electrolyte was 0.2 M HCl. The repeatability, linearity, accuracy, interference effects of foreign ions, pH, and the limit of detection of the procedure were also studied. The performance of the gold electrode (AuE) was evaluated, demonstrating a low limit of detection (LOD), greater reproducibility, and higher sensitivity to Hg in water samples. A detection limit of 0.06 ng/mL was achieved with a preconcentration time of 600s. The reproducibility, expressed as relative standard deviation (RSD), was always less than 1.62%. The method demonstrated good selectivity and was successfully applied to detect Hg in fresh and wastewater samples collected from various locations within the study area.

**Keywords:** Hg, water samples, Gold electrode, Anodic stripping voltammetry

## 1. Introduction

Mercury (Hg) is of particular concern among hazardous heavy metals due to its high volatility and neurotoxicity. Hg can enter the human body through inhalation of its vapors (primarily Hg<sup>0</sup>), ingestion of contaminated drinking water (mostly Hg<sup>2+</sup>), and consumption of fish and seafood (largely methylmercury)[1-5]. Rapid industrialization, agricultural practices, and improper waste disposal have significantly contributed to Hg contamination of surface and groundwater resources, particularly in developing regions [5-10]. In provinces such as Sindh, Pakistan, where industrial, urban, and agricultural areas coexist, assessing Hg levels in water bodies is essential for environmental protection and public health management. The detection of trace metals such as Hg requires highly sensitive and selective analytical techniques. Conventional methods, including cold vapor atomic absorption spectrophotometry (CVAAS) and cold vapor atomic fluorescence spectrophotometry (CVAFS), are widely used for the determination of highly toxic methylmercury in environmental samples. Other techniques, such as atomic absorption spectrometry (AAS), inductively coupled plasma mass spectrometry (ICP-MS), and atomic fluorescence spectrometry, offer excellent detection capabilities; however, they often involve high operational costs, complex instrumentation, and extensive sample preparation[11-13].

In contrast, electroanalytical techniques, particularly anodic stripping voltammetry (ASV), have gained considerable attention for their simplicity, low cost, and ability to detect metals at ultratrace levels with high sensitivity. ASV is based on preconcentrating metal ions at an electrode surface, followed by electrochemical stripping, which generates a current proportional to the analyte concentration. Among various electrode materials, gold electrodes exhibit a strong affinity for mercury through amalgam formation, thereby enhancing detection sensitivity. Recent advancements in modified gold electrodes, particularly those incorporating nanomaterials, have significantly improved detection limits and selectivity for mercury ions. Several studies have demonstrated that gold nanoparticle-modified electrodes provide excellent analytical performance for Hg detection, enabling quantification at trace and ultra-trace levels. These developments highlight the potential of electrochemical methods as practical and efficient tools for environmental monitoring[14-17].

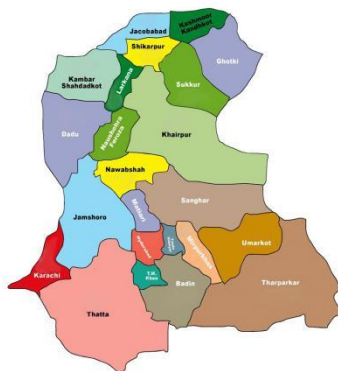
In this context, the present study focuses on the detection of Hg in water samples collected from various districts of Sindh, Pakistan, using a modified gold electrode coupled with anodic stripping voltammetry. The aim is to evaluate the analytical performance of the proposed method and to assess Hg contamination levels in the collected samples. The work also investigates the optimum conditions for the detection of total mercury in water samples for Hg(II) determination by DPASV and compares them with those of the conventional technique

## 2.0. Materials and Methods

### 2.1. Sampling and Pretreatment

Water samples were collected from different districts of Sindh, Pakistan. (Fig 1) including industrial, agricultural, and residential areas. A total of 60 (fresh and wastewater) samples were collected from 48 sampling points across different areas of the district of Hyderabad, as mapped by the Global Positioning System (GPS). Jamshoro, district. Dadu district,

Naushero Feroz, and the district. Khairpur Mirs is located in the Sindh province of Pakistan, according to the Global Positioning System (GPS).



**Figure 1: Global Positioning System (GPS) of the district of Hyderabad, Jamshoro, district. Dadu district, Naushero Feroz, and the district. Khairpur Mirs**

The water samples were collected from the main stream at five to six different sampling points at a depth of 20–30cm due to low flow conditions and industrial, agricultural, and residential areas. The samples were collected in Van Dorn plastic bottles (1.5 liters) and stored in well-stoppered polyethylene bottles that had been previously soaked in 10% nitric acid for 24 h and rinsed with ultra-pure water. Collected water samples were stored in an ice box and transported to the laboratory on the same day. When organic matter was present, samples were digested with nitric acid (pH < 2 to prevent metal adsorption on container walls) under controlled heating conditions to ensure complete dissolution of Hg species. Five to six samples from each site were combined in a washed plastic bucket to form a composite sample, which was then filtered through a 0.45  $\mu\text{m}$  filter paper under vacuum and stored at 4 °C until further processing and analysis. Additionally, physico-chemical parameters such as water temperature, pH, electrical conductivity (EC), and total dissolved solids (TDS) were measured in the field using a thermometer, a pH meter (781-pH meter, Metrohm), and a conductivity meter (InoLab Cond 720, Germany), respectively.

## 2.2 Chemicals and Reagents

All chemicals used in this study were of analytical grade and used without further purification. A standard stock solution of mercury(II) ions ( $\text{Hg}^{2+}$ , 1000 mg/L) was prepared from mercuric chloride ( $\text{HgCl}_2$ ) in deionized water. Working standard solutions were obtained by appropriate dilution of the stock solution. Supporting electrolyte solutions, such as acetate buffer (0.1 M), were prepared using acetic acid and sodium acetate to maintain the desired pH during analysis. Nitric acid ( $\text{HNO}_3$ ) was used for sample preservation and, where necessary, for digestion. All glassware was thoroughly cleaned with dilute nitric acid and rinsed with deionized water prior to use.

## 2.3. Instrumentation

Electrochemical measurements were carried out using an anodic stripping voltammetry (ASV) system connected to a potentiostat/Galvanostat. A conventional three-electrode cell configuration was employed, consisting of a modified gold electrode as the working electrode, an Ag/AgCl electrode as the reference electrode, and a platinum wire as the counter electrode. All measurements were conducted at room temperature under controlled laboratory conditions.

## 2.4. Preparation of Modified Gold Electrode

The gold electrode was modified using an appropriate surface treatment method (e.g., electrodeposition or chemical modification) to enhance its sensitivity toward  $\text{Hg}^{2+}$  ions. Prior to modification, the electrode was mechanically polished with an alumina slurry (0.05  $\mu\text{m}$ ) on a polishing cloth to obtain a mirror-like surface. It was then thoroughly rinsed with deionized water and sonicated to remove any residual particles. Electrochemical cleaning was performed by cycling the electrode in dilute sulfuric acid until a stable voltammogram was obtained. After modification, the electrode was rinsed and stored in deionized water when not in use.

## 2.5. Anodic Stripping Voltammetry Procedure

The determination of mercury was performed using anodic stripping voltammetry. A measured volume of the sample or standard solution was transferred into the electrochemical cell containing the supporting electrolyte.

The analysis involved two main steps:

**Deposition step:** Mercury ions were preconcentrated on the surface of the modified gold electrode at a fixed deposition potential, with constant stirring for a specified time.

**Stripping step:** After a rest period, the deposited mercury was oxidized (stripped) by scanning the potential in the positive direction, producing a current peak proportional to the mercury concentration.

Experimental parameters, including deposition potential, deposition time, scan rate, and pH of the supporting electrolyte, were optimized to achieve maximum sensitivity and reproducibility.

## 2.6. Calibration and Quantification

Calibration curves were constructed using standard Hg solutions of known concentrations under optimized conditions. The peak current obtained from ASV measurements was plotted against Hg concentration to establish linearity. Hg concentrations in water samples were determined by comparing their peak currents with the calibration curve (Fig. 2).

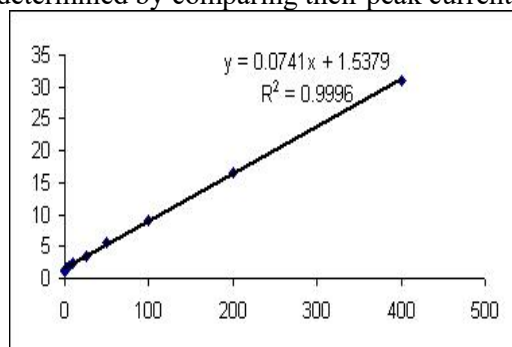


Figure 2: Calibration plot of  $2 \times 10^{-10}$  M to  $2 \times 10^{-6}$  M Hg solution

To validate the method, recovery studies were performed by spiking selected samples with known amounts of mercury. Replicate measurements were carried out to assess precision and accuracy.

## 2.7. Quality Control and Data Analysis

All experiments were conducted in triplicate, and results were expressed as mean  $\pm$  standard deviation. Blank measurements were performed to account for background signals. Detection limits were calculated based on signal-to-noise ratio criteria. Data analysis and graphical representations were carried out using appropriate software

## 2.8. Voltametric studies

A volume of 10 mL flask solution containing 100  $\mu\text{g/L}$  (prepared from 1000 mg/L stock solution), in 0.2M HCl electrolyte (2 mL of 0.2M HCl) was transferred into a polarographic cell. After purging the solution with Nitrogen for 5 min. Voltammograms were taken by scanning the potential range from 0.3v to 0.8v at a voltage step of 1.1 s, drop size 1, pulse amplitude of 0.05V, pulse time of 0.04s, voltage step of 0.004 v/s, scan rate 0.0397v/s, deposition potential of 0.0 v, equilibrium time of 10 s, stirring rate 3000 rpm, and  $\text{N}_2$  pressure of 0.5Kg  $\text{cm}^{-2}$  (0.49 bar). All the measurements were performed at room temperature ( $25 \pm 5$  C $^\circ$ )

## 3.0 Results and Discussion

A modified gold electrode was selected for the proposed study because it offers greater sensitivity to Hg(II) than other electrodes. Six samples of certified reference material and a triplicate sample of each real water sample (5mL) were taken in a cell, and 2 mL of 0.2 M HCl was added for quantification of Hg in the water samples.

### 3.1. Electrochemical Behavior of Mercury at the Modified Gold Electrode

The electrochemical response of  $\text{Hg}^{2+}$  at the modified gold electrode was investigated using differential pulse anodic stripping voltammetry (DPASV). A well-defined anodic stripping peak was observed at approximately +0.05 V (vs. Ag/AgCl), corresponding to the oxidation of Hg deposited on the electrode surface. Compared to the bare gold electrode, the modified electrode exhibited a significantly enhanced peak current and sharper peak shape, indicating improved electron transfer kinetics and increased active surface area. This enhancement can be attributed to the strong affinity between gold and Hg, facilitating amalgam formation and efficient preconcentration.

### 3.2 Optimization of Experimental Parameters

#### 3.2.1 Effect of Deposition Potential

The deposition potential was optimized in the range of  $-0.20$  to  $+0.60$  V. The peak current increased gradually (Fig. 3) with increasing positive potential, reaching a maximum at  $+0.30$  V. Beyond this value, the current decreased due to hydrogen evolution and other competing side reactions, leading to signal instability. Therefore,  $+0.30$  V was selected as the optimum deposition potential for efficient  $\text{Hg}^{2+}$  accumulation. This indicates that 0.30 V is optimal for efficient Hg accumulation.

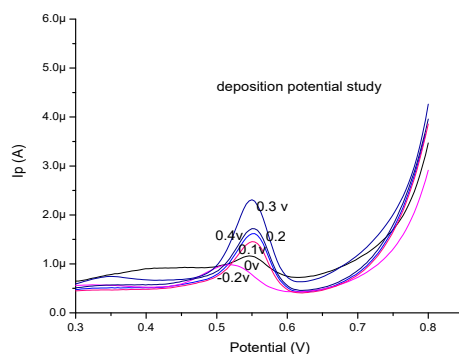


Figure 3: Effect of deposition potential on  $I_p$  of Hg.

### 3.2.2. Effect of deposition Time

The effect of deposition time was also investigated using DPASV at 10–120 s in unstirred solutions, and the corresponding effect on peak potential is presented in Figure 4 reaching a maximum at 120 s. indicating that the peak current increased with increasing deposition time, indicating effective accumulation of  $\text{Hg}^{2+}$  ions on the gold electrode surface. At longer deposition times, the response gradually approached a plateau, suggesting saturation of the available active sites. Due to Hg's high solubility in gold, excessive deposition may lead to non-linear behavior and reduced analytical performance. The maximum peak current with a well-defined peak shape was obtained at 120 s. Beyond this time, the peak current decreased, and the peaks became broader and shifted toward more positive potentials, indicating surface saturation and reduced current efficiency. Therefore, a deposition time of 2 min was selected as the optimum condition for subsequent studies, as it provided sufficient mercury accumulation while maintaining good peak shape and oxidation efficiency (Fig.4).

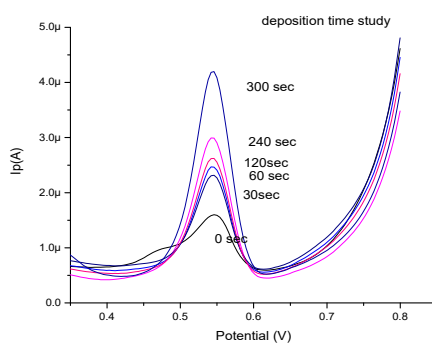


Figure 4: Effect of deposition Time on  $I_p$  of Hg.

### 3.2.3. Effect of pH

The influence of the hydronium ion ( $\text{H}^+$ ) concentration on the accumulation process was examined over a (2.0-12) pH range using 0.1M sodium hydroxide (NaOH). Maximum peak current was observed at pH 4 (Table 1).

Table 1: Effect of Change in H-ion concentration

pH	2	3	4	5	6	7	8	9	10	11
$I(\mu\text{A})$	5.3	6.8	12	8.5	3.2	2.6	1.3	1.7	1.3	1.1

The bell-shaped curve indicates that at lower pH, proton competition reduces mercury deposition, while at higher pH, hydrolysis of  $\text{Hg}^{2+}$  decreases free-ion availability (Fig. 5), pH 4 was selected for the entire study because it yielded the best results, with the highest peak current. The differential pulse voltammograms were obtained following preconcentration in solutions containing 100 ppb  $\text{Hg}^{2+}$  at different pH (Fig.5). At pH under 4.0, the height of peaks decreased very sharply, and no peak was observed from preconcentration at pH 12.0. The maximum peak height was observed at pH 4.0; however, since the method showed better tolerance to interfering ions at this pH, this pH was preferred throughout this work. At low pH values, the complexation reaction between  $\text{Hg}^{2+}$  ions and the modifier is less effective because the organic ligands undergo protonation. At high pH values, the hydrolysis of Hg (II) interferes with the accumulation, and the modifier can be split from the electrode surface through alkaline cleavage

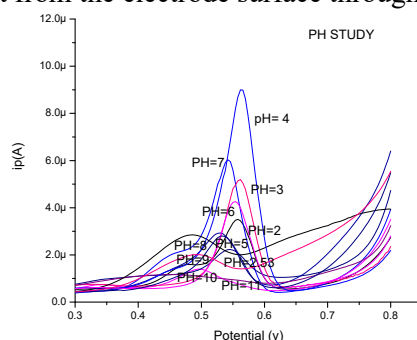


Figure 5: Effect of pH on  $I_p$  of Hg.

### 3.2.4. Effect of Concentration of electrolyte

The stripping voltammograms of  $\text{Hg}(\text{II})$  (100 ppb) were compared using three supporting electrolytes, 0.2 M HCl,  $\text{HClO}_4$ , and  $\text{HNO}_3$ . Among them, HCl produced the highest and sharpest peak current and was therefore selected as the optimal electrolyte (Fig. 6). The Effect of HCl volume (1–6 mL) was further investigated in the presence of 100  $\mu\text{g}/\text{L}$   $\text{Hg}(\text{II})$ . The best response was obtained with 2 mL of 0.2 M HCl, which showed a well-defined peak shape, lower residual current, and a shift of peak potential toward lower values. The supporting electrolyte strongly influenced the electrochemical dissolution of Hg from the gold electrode. Increasing the HCl concentration from 0.01 to 0.2 M enhanced the peak current, while the mercury stripping peak shifted from 0.61 to 0.68 V. Although residual current also increased, 0.2 M HCl

provided the best balance of sensitivity, peak separation, and signal stability. The presence of chloride ions also shifted the mercury stripping peak to more negative potentials, reducing peak distortion and background interference. Background current decreased at lower HCl concentrations; however, 0.2 M HCl was finally selected because it produced a sharp oxidation peak for mercury at approximately 0.3 V with low residual current and good reproducibility. The sharp voltammetric response confirmed the high efficiency of the gold electrode for Hg detection. The results obtained by anodic stripping voltammetry were in excellent agreement with the conventional CVAAS method, while the voltammetric technique showed higher sensitivity (Fig. 6 & 7).

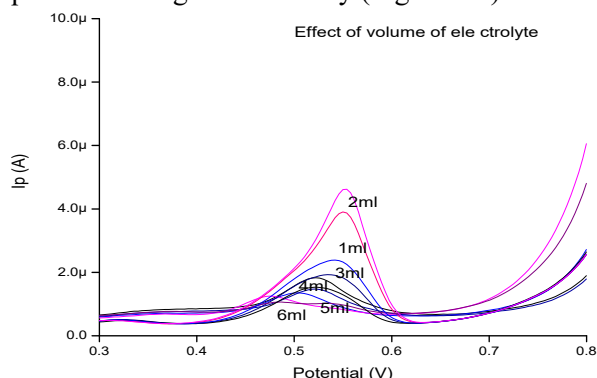


Figure 6: Effect of electrolyte on peak current of Hg ions

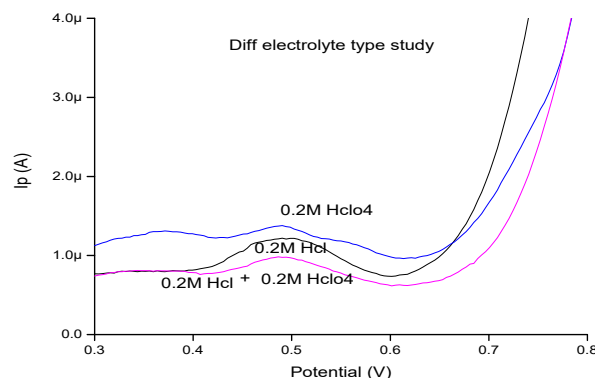


Figure 7: Effect of electrolyte on peak current of Hg ions

### 3.2.6. Stirring rate study

The effect of stirring rate was studied in the range of (0-3000 rpm) at an interval of 200 rpm. It was observed that the peak signal enhanced gradually with every increase of 200 rpm, and consequently, the best response was achieved at 3000 rpm, so it was selected as the optimal stirring rate for other succeeding parameters study (Fig. 8), similar to the study of Niaz et al [25]

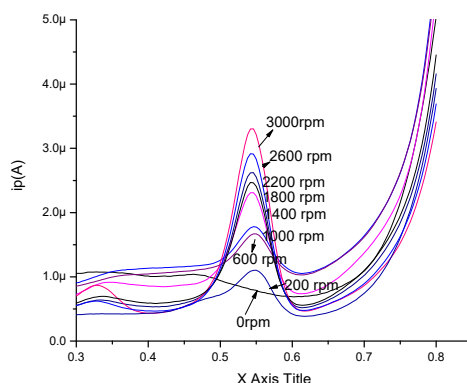


Figure 8: Effect of stirring rate on peak current of 100 ppb Hg solution

### 3.2.7. Reproducibility study.

Reproducibility (stability) was checked by recording 18 successive measurements for the same standard solution (100 ppb) of mercury containing 0.2 M HCl as supporting electrolyte using the proposed procedure (Fig. 9). The electrode showed good reproducibility with an RSD of 1.62%. No surface fouling was observed, and the electrode was renewable and reproducible, with no need for polishing or sonication. This study proves excellent stability for Au electrode in our developed method.

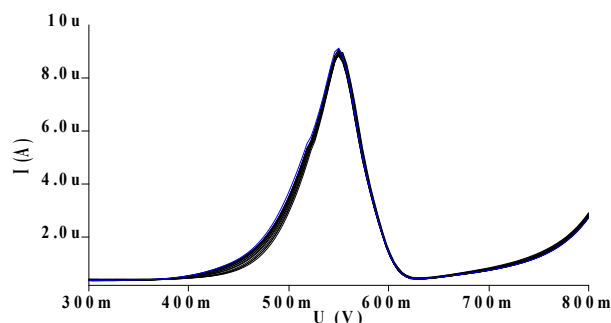
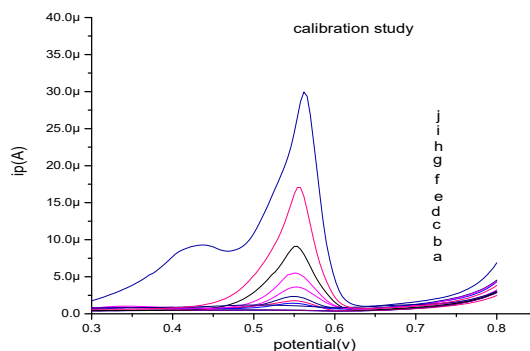


Figure 9: Effect of reproducibility on peak current of 100 ppb Hg solution

### 3.2.8. Linear calibration curves study at the gold electrode

The calibration plots for all studied mercury analytes by DPV at a solid-gold electrode were investigated. Calibration plots were obtained under optimized conditions using DPV for a 0.1 mol.L<sup>-1</sup> mercury solution. The peak current was

linearly proportional to the concentration in the range from  $5 \times 10^{-10}$  mol.L<sup>-1</sup> and  $2 \times 10^{-6}$  mol.L<sup>-1</sup>. The calibration curve (Fig. 10) showed good linearity between concentration and peak current over the entire concentration range. This indicated that, by promoting oxidation, the electrode surface remained unblocked even at this high concentration range. This suggested that the method could be applied to a broad range of concentrations. LOD was determined by the relation,  $3 \cdot \text{SD}/\text{SLOPE}$ , and found as 0.06  $\mu\text{g/L}$ . The calibration range and limit of detection (LOD) of our newly developed method for the determination of total Hg are better than those reported by Barbosa et al., [2], who described a range of  $2 \times 10^{-6}$  M to  $2 \times 10^{-10}$  M and an LOD of 0.06  $\mu\text{mol.L}^{-1}$  for Hg using DPASV. This developed method is robust, more sensitive, selective, and economical than the previously reported official methods, such as CVAAS, ICP-MS, AES, AFS, and HPLC [17-25]. The calculated limit of detection (LOD) was 0.065  $\mu\text{g/L}$ , demonstrating the capability of the method for trace-level mercury detection. This sensitivity is comparable to more sophisticated techniques while maintaining lower cost and operational simplicity.



**Figure 10: DPAS voltammograms of mercury (calibration curve) at gold electrode in 0.1 mol L<sup>-1</sup> mercury standard solution; (a) 0 (blank), (b)  $2 \times 10^{-10}$  M, (c)  $5 \times 10^{-9}$  M, (d)  $2 \times 10^{-8}$  M, (e)  $1 \times 10^{-7}$  M, (f)  $2 \times 10^{-7}$  M (g)  $5 \times 10^{-7}$  M (h)  $10 \times 10^{-7}$  M (i)  $1.0 \times 10^{-6}$  M (j)  $2 \times 10^{-6}$  M**

The results demonstrate that the modified gold electrode significantly enhances the sensitivity and selectivity of anodic stripping voltammetry for mercury detection. The method provides reliable quantification of trace Hg in complex water matrices and reveals concerning levels of contamination in certain districts of Sindh. The combination of low detection limit, good reproducibility, and successful application to real samples confirms the suitability of this approach for routine environmental analysis.

The optimum conditions for electroanalytical determination of mercury in the presence of 0.2 M HCl by means of deposition followed by DPASV voltammetry were found to be the following: Mod: Amplitude 25 mV, scan rate 10 mV/s, deposition time 3 min, and deposition potential 0.0V. under these conditions, the peak height as a function of analyte mercury concentration in the presence of 0.02 M mercuric nitrate and 0.2 M HCl in 3:2 M/W is linear of both low and high concentrations in the range from  $4.54 \times 10^{-7}$  to  $3.63 \times 10^{-6}$  and  $4.54 \times 10^{-5}$  to  $3.63 \times 10^{-4}$  mol.L<sup>-1</sup> mercury with the regression coefficient  $R^2 = 0.9984$  and regression equation of  $I(\mu\text{A}) = 0.7377C(\text{M}) + 6.0067$ . This shows that the method is suitable for determining mercury over a broad concentration range without surface fouling. The limit of detection was calculated from the calibration plot [29]. The detection limit is the analyte concentration that yields a signal equal to the blank signal,  $Y_b$ , plus three times the standard deviation of the blank,  $S_b$  ( $Y = Y_b + 3 \cdot S_b$ ). From this equation, a LOD of 0.06  $\mu\text{g/L}$  for mercury is calculated, indicating the proposed method's good sensitivity.

### 3.3. Interference study

Interference studies were conducted to evaluate the selectivity of the proposed method by adding various metal ions to tap water samples spiked with Hg(II) (100  $\mu\text{g/L}$ ). The effects of different cations and anions were investigated at a fixed Hg(II) concentration of 100 ppb in the presence of known concentrations of foreign ions. Mercury concentration was determined experimentally using a calibration curve. The tolerance limit for interfering species was defined as a signal variation within  $\pm 5\%$ . All tested ions remained within this limit, except selenium, which interfered due to oxidation at a potential similar to that of mercury. However, selenium is used only as an inhibitor in polymeric industries and is not expected to be present in the analyzed samples. These results demonstrate the method's good selectivity, with no significant interference from other metallic ions (Table 2).

**Table 2: Effect of the presence of different foreign ions on the determination of Hg(II) concentrations [Hg(II)] = 100 ppb, pH 4. Interference studies for different cations.**

Interferent	Added concentration ( $5 \times 10^{-7}$ M) [Hg <sup>2+</sup> ] (100ppb)	Tolerance limit ( $\mu\text{g/L}$ )	Standard deviation
Pb <sup>2+</sup>	1 : 5	500	3.2±0.02
Ag <sup>+</sup>	1 : 50	5000	2.8±0.01
Sn <sup>2+</sup>	1 : 50	5000	3.2±0.02
Cd <sup>2+</sup>	1 : 10	1000	3.5±0.03
Cu <sup>2+</sup>	1 : 5	500	3.4±0.02
Zn <sup>2+</sup>	1 : 20	2000	4.2±0.01
Mg <sup>2+</sup>	1 : 10	1000	3.1±0.02

Cr <sup>6+</sup>	1 : 20	2000	3.2±0.02
Al <sup>3+</sup>	1 : 20	2000	3.8±0.01
Co <sup>2+</sup>	1 : 30	3000	2.5±0.03
Ni <sup>2+</sup>	1 : 20	2000	1.82±0.03
NO <sub>3</sub>	1 : 10	1000	3.2±0.02
SO <sub>4</sub>	1 : 10	1000	2.5±0.01
Br <sup>-</sup>	1 : 5	500	3.2±0.02
As <sup>3+</sup>	1 : 20	2000	2.84±0.01
V <sup>3+</sup>	1 : 200	20000	3.5±0.02
Ca <sup>2+</sup>	1 : 20	2000	2.95±0.03
Na <sup>+</sup>	1:100	10000	3.2±0.02
F <sup>-</sup>	1:100	10000	1.6±0.02

### 3.4.Recovery test

In order to prove the validity of proposed method further, voltammetric recovery test was performed by spiking tap water samples with standard mercury compounds the % recovery under the combined matrix effect of all foreign ions like, Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Pb<sup>2+</sup>, Ni<sup>2+</sup>, As<sup>3+</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, CO<sub>3</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>, etc was carried out (Table 3). A recovery range of 98–100.8% Hg strengthens the feasibility of the developed method, in addition to the above-mentioned comparison.

**Table 3: Recovery test showing comparison between added and recovered amount of Hg after spiking**

MERCURY added ( $\mu\text{mol L}^{-1}$ )	Found ( $\mu\text{mol L}^{-1}$ )	Difference ( $\mu\text{mol L}^{-1}$ )	Recovery (%)
0.0	1.68	1.68	-
1.0	2.66	0.98	98.0
2.0	3.66	1.98	99.0
5.0	6.72	5.04	100.8
10.0	11.50	9.82	98.2

It is clear from Table 3 that the results obtained by the method is quite close at low concentrations of Hg. However, as the dilution factor decreases and the final concentration in the product increases, greater differences in the results are observed [4,24]. It's indicated that this method is more valid for lower concentration (trace level) determination and quantification of Hg from environmental samples. As the permissible exposure limit (PEL) for mercury is 1-2  $\mu\text{g/l}$  [5]. Therefore, the exposure of mercury to the local population is an environmental issue of great concern regarding the transfer of mercury by oral routes in children and adults with the same ratio, causing manifold toxicity and health problems in underdeveloped countries like Pakistan. The results showed an alarming level of Hg in the observed water samples from the study area and in similar environmental products. Sufficient amounts of these toxic compounds, mercury (Hg), accumulate in human bodies and severely affect body systems, causing complex diseases and disorders[15-20]

### 3.5. Validity of developed method (Application to sample analysis)

To validate the analytical applicability of the newly developed method, recovery experiments were conducted using spiked water samples containing Hg<sup>2+</sup> ions along with other metal ions. The results obtained by the proposed method are presented in Table (4) and were compared with those obtained using the officially reported method. The validity of the developed method for Hg determination in water samples, using a modified electrode after microwave-assisted acid digestion with 0.1 M H<sub>2</sub>SO<sub>4</sub> as the supporting electrolyte, has also been reported by other researchers [27,28]

**Table 4: Comparison of Hg determination in various water samples by developed and official methods.**

S. No.	Sample type	By develop methodn	By reported methods [27,28]
1	Drinking water	2.3±0.1 ppb	2.5±0.2 ppb
2	Tap water	5.2±0.2 ppb	5.7±0.4 ppb
3	Indus river water	6.2±0.4 ppb	6.9±1.4 ppb
4	Ground water	5.8 ±0.3 ppb	6.1 ±0.2 ppb

n =Average of 3 results, ±Std. Dev.

### 3.6. Application of the Proposed method at Industrial Scale

The developed method was effectively applied to the determination of mercury in fresh and waste water samples from industrial discharges in the Jamshoro district of Sindh province. Mercury concentration was determined by the standard addition method, with results checked at the 95% confidence interval (n=6). The proposed method was applied to industrial waste discharge samples containing mercury, and the results were compared with those obtained by AAS spectrometry, as shown in Table 5.

**Table 5: Analysis of industrial effluents samples containing our proposed method (DISTT. JAMSHORO).**

Sample DPASV	1	2	3	4	5	6	7	8	9	10
proposed method (ppb)	8.77±0.01	14.22±0.02	7.36±0.02	2.45±0.02	2.32±0.01	1.28±0.01	2.08±0.02	3.18±0.02	not found	3.18±0.02

N= no. of replications; <sup>a</sup>, average of 3 values ±, standard deviation

The proposed method has several distinct advantages over previously reported CV-AAS methods, which involved preconcentration and extractive separation steps prior to analysis and required large volumes of samples. In the present method, the analysis time is only 30 sec, without the use of any costly solvents, complicated operating procedures, or sophisticated instrumentation protocols. The novelty of the present method is that the results obtained with DPASV are comparable to those from AAS methods. The developed method was applied to diluted samples of various water products, using the optimized parameters. The results obtained using this method are in good agreement with those reported earlier [10-21], which proves the validity of the developed method (Table 6).

**Table 6: % recovery study for validation of proposed method for the detection of Hg from water samples**

Certified reference material( CRM)	Added Hg <sup>+2</sup>	Obtained Hg <sup>+2</sup>	%recovery
NSSS-3	10 ng/mL		98.2%

#### 4.0 Conclusion

The detection of Hg concentration in water samples, as a highly toxic heavy metal, was carried out using a newly developed gold electrode method. The procedure was successfully applied to real samples to check the method's selectivity and sensitivity. The method proved highly selective, sensitive, cost-effective, robust, and economical, with rapid analysis time and high accuracy and precision for the determination of mercury at trace and ultra-trace levels in aqueous media. The proposed method is very sensitive, efficient, selective, simple, cost-effective, robust, and environmentally friendly, owing to its very low consumption of hazardous chemicals for the trace and ultra-trace level determination of mercury in aqueous matrices. In addition, it emits no hazardous chemicals into the atmosphere that may harm our serene environment or disrupt our natural atmosphere. From this study, it is concluded that (i) the current proposed procedure deposition followed by DPASV anodic voltammetry is a simple and efficient strategy for the detection of Hg from environmental water samples by using a gold electrode, which shows extra stability and an excellent reproducibility for routine electroanalysis of Hg. (ii) Monolayer coverage of Hg at the surface of the gold electrode made the electron-proton transfer easier without inhibiting the electrode kinetics. So it would be important for future research to investigate the electrooxidation of various organic compounds on such surfaces, as this increases the electrochemical response rather than preventing the electrode reaction.

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#### Author's Contribution:

Abdul Sattar Soomro (Ph.D. scholar): Investigation, data curation, Dr. Sirajuddin (assisted in the experiment), Prof. Dr. Tasneem Gul Kazi (Co-Supervisor): review, validation, Prof. Tasneem Gul Kazi (Co-Supervisor): Visualization, editing, Prof. Dr. Mushtaque Ali Jakhriani (Supervisor of the Ph.D Project): Conceptualization, investigation, methodology, formal analysis, data curation, validation, writing original draft, editing.

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