Gold–Copper Film Electrode for Voltammetry Determination of Mercury in Water

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Gold-copper film electrode prepared in situ on carbon paste solid disk substrate (Au–CuF/CPE) was studied as a working electrode. The factors influencing mercury stripping peak currents, such as $C_{\text{Au(III)}}$, $C_{\text{Cu(II)}}$, type of acids and their concentration ($\text{HClO}_4$, 0.005 M), deposition potential (-800 mV) for Au–CuF/CPE, deposition time (180 s), and interferents, were investigated and optimized. The method has a low limit of detection of 0.13 μg/L and is not affected significantly by the examined ions/substance. It was applied to detect the concentration of Hg in real water samples and is promising for practical usage.

1. Introduction

Among heavy metals, mercury (Hg) is one of the most toxic and can be harmful to the brain, kidney, nervous system, and endocrine system in humans and animals [1, 2]. Moreover, the toxicity of Hg is high even at low concentrations because it can accumulate and amplify biologically [3, 4]. Therefore, the standards and guideline values for Hg in drinking water recommended by the World Health Organization and the Environmental Protection Agency are 1 and 2 μg/L, respectively [5, 6]. Therefore, the development of a simple and reliable method for monitoring Hg concentrations in water is of great significance. To determine the trace (less than mg/L) and super trace (less than μg/L) amount of Hg, cold-vapor atomic absorption spectroscopy or cold-vapor atomic fluorescence spectrometry and inductively coupled plasma-mass spectrometry have been used [6, 7]. Although these methods are highly sensitive, their analytical procedures and equipment systems are relatively complex and costly [8, 9]. Currently, numerous studies show that it is possible to determine Hg by using stripping voltammetry, specially anodic stripping voltammetry (ASV). This method possesses several advantages, such as high sensitivity, simple test operation, and low cost of equipment and analysis [8, 9]. A proper working electrode is an important requirement for trace and super trace ASV methods. Gold electrodes (AuE) [10], gold film electrodes (AuFE) [3, 11–13], and modified gold electrodes are often used to determine Hg because gold has a strong affinity for Hg thus facilitating mercury preconcentration on the electrode surface [9].Recently, several researchers have used copper film electrodes (CuFE) for trace mercury detection in combination with ASV using glassy carbon electrode [12] or boron-doped diamond electrode (BDD) [14, 15]. According to Jovanovski and Hrastnik [15], CuFE exhibits excellent stripping performance comparable or even surpassing that of the gold electrodes for trace mercury determination. The authors also pointed out some attractive properties of CuFE such as simple electrochemical preparation, high sensitivity, well-defined and undistorted stripping signals, and much cheaper than gold film electrodes.
With the aim of developing a low-cost method to determine trace levels of mercury in natural water, based on previously published works in the literature, preliminary tests with stripping voltammetry using glassy carbon and paste carbon electrodes coated with Au or Cu film have been conducted. Attempts using Au or Cu film electrodes in electrolytes containing various types of acid revealed that well-defined stripping peak of Hg appeared constantly on the AuFE but not on the CuFE. In the case of using Au-Cu film formed in situ, the stripping signals for Hg are relatively stable and sensitive. This paper presents the use of gold–copper films on paste carbon working electrode to determine the trace amount of Hg in water.

2. Experimental

2.1. Chemicals and Equipment. Mercury and copper standard solutions (1000 mg/L) were purchased from Merck. HAuCl₄·3H₂O, 37% HCl, 70% HClO₄, ≥65% HNO₃, and 30% (w/w) H₂O₂ were from Sigma-Aldrich. Graphite powder with a particle size of less than 20 μm and paraffin oil (Sigma-Aldrich) were used to prepare carbon-paste electrodes. All glassware was thoroughly cleaned by soaking into a 1:2 (v/v) HNO₃/H₂O solution for 4–6 h and rinsed with double-distilled water (ddH₂O) before use.

Anodic stripping voltammetry measurements were performed on 797 VA Computrace (Metrohm, Switzerland) with a 50 mL glass electrochemical cell and a system of three electrodes, namely, a carbon paste electrode as working electrode, an Ag/AgCl (3 M KCl) as the reference electrode, and a platinum rod as the counter electrode.

Water samples were digested using 705 UV Digester (Metrohm, Switzerland).

2.2. Working Electrode Preparation

2.2.1. Substrate Electrode. For the carbon paste electrode preparation (CPE), a hollow Teflon housing having an inner diameter of 3.0 mm with a stainless wire of 1 mm in diameter was tightly filled with a paste prepared from a mixture of graphite powder and paraffin oil (6:4, w/w). The surface of the electrode was gently polished on a clean glossy paper to create a flat surface, rinsed with ddH₂O, and dried naturally at room temperature.

2.2.2. Working Electrode. Gold/copper film were in situ electrochemical plated on a carbon paste substrate electrode (designated as AuF/CPE, CuF/CPE, and Au-CuF/CPE) from solutions containing Au(III) or/and Cu(II). During the deposition step of the anodic stripping voltammetry, these metal ions were reduced and accumulate on the electrode surface at a defined potential and time. In this step, working electrode rotates at a constant speed.

2.3. Differential Pulse Anodic Stripping Voltammetry Measurements. Working electrode, reference electrode, and counter electrode were immersed into the electrochemical cell. The deposition step was carried out at a potential of -1100 mV (E(dep)) in the solution containing HClO₄, Hg(II), Au(III) (or Cu(II), or a mixture of Au(III) and Cu(II)). Deposition time (t(dep)) was set at 180 s for the CP-substrate electrode. A rotating speed (ω) of 2000 rpm was applied for all kinds of working electrode used in this work. During the deposition step, Au(III), Cu(II), and Hg(II) were reduced to element forms and accumulate on the electrode surface.

At the end of the deposition step, stirring was stopped for 5–15 s (t(equil) equilibrium time) while keeping the potential on the working electrode. After the equilibrium time, the voltammograms were recorded at a differential anodic stripping potential scan from -100 mV to 1000 mV with a constant scan rate of 15 mV/s⁻¹. At the end of each scan, the surface of the electrode was cleaned by applying a potential of +600 mV (E(clean) for 20 s (t(clean)) to completely remove remaining Hg from the electrode surface. Stripping peak potential (Eₛ) and stripping peak current (Iₛ) were determined from the voltammograms. On the differential pulse stripping voltammogram, two stripping peaks appeared corresponding to the oxidation processes of Cu and Hg (to CuII and HgII) at the potentials of approximately 0.2 V and 0.65 V.

2.4. Sample Analysis. Composite river/lake water samples were taken: two one-liter samples were taken at a distance of about 20 meters from the bank at a depth of 50 cm across the river at a location of sampling. These samples were then mixed to make a composite sample. Well-water samples were taken directly from a water pump 15 minutes after the first water was discharged to ensure that it is truly from the depth. The samples were acidified with concentrated HNO₃ (2 mL HNO₃·L⁻¹ sample) and stored in clean glass bottles placed in a refrigerator at 4°C prior to analysis [16].

In natural water, Hg may exist in various forms, and therefore, the samples were digested before determining total HgII. Specifically, 10 mL of the sample was put into a quartz cuvette with a lid, containing 30 μL of 30% (w/w) H₂O₂, and digested with a 705 UV Digester with a 500 W UV light source at 90°C for 90 min. After complete decomposition, all forms of Hg in the sample are converted to HgII (or total Hg) [16]. The digested sample was filtered through a 0.45 μm glass-fiber filter to remove suspended solids. The filtered sample was analyzed on the 797 VA Computrace electrochemical analyzer (Metrohm). Unanalyzed water samples were preserved in the refrigerator at 4°C for no more than 14 days.

3. Results and Discussion

3.1. Stripping Signal of HgII at Copper Film Electrodes. Unlike previously published results [12, 15], the stripping signals of Hg at both CuF/GCE (copper film on glassy carbon electrode) [17] and CuF/CPE electrodes in situ prepared were not observed despite changing different analytical conditions, such as acid type and its concentration (HNO₃, HCl, and HClO₄), the CuII concentration (C[CuII]) from 0.1 mg/L to 0.5 mg/L, and different electrochemical conditions (E(dep) and t(dep)).
to the solution must be \( \geq 3.3 \). However, in order to achieve better repeatability of the performance of the AuF/CPE electrode. Overall, the increase of Au concentration, while relative standard deviation (RSD) decreases, indicating increasing repeatability (Figure 2). However, the increase of Au(III) to be added decreases, indicating increasing repeatability (Figure 2). However, the increase of \( \text{Hg(II)} \) solution (in HClO₄ acid medium) does not contain Cu(II), no peak appears on the differential pulse anodic stripping voltammograms (DP-ASV curve), while if Cu(II) is added to the solution, a stripping peak of the Cu appears at a potential of about 0.2 V. In both cases, no stripping peak of Hg is obtained. During anodic scanning, Cu film on the electrode surface is mostly oxidized and dissolved (at about 0.2 V) before the oxidation of Hg(0) (at about +0.65 V) that releases much of Hg(0) accumulated on the Cu film layer of electrode surface to the solution. This might be the reason why stripping peak of Hg does not appear on the examined electrodes.

3.2. Influence of Au(III) Concentration on Performance of Gold Film Electrodes. The concentration of Au(III) \( (C_{\text{Au(III)}}) \), 0.1–0.5 mg/L in the solution containing HClO₄ affects the performance of the AuF/CPE electrode. Overall, \( I_p \) increases with Au concentration, while relative standard deviation (RSD) decreases, indicating increasing repeatability (Figure 2). However, the increase of \( I_p \) and decrease of RSD are faster at the \( C_{\text{Au(III)}} \) between 0.1 and 0.2 mg/L (Figure 2). According to [18], at a Hg(II) concentration of 5 mg/L, the standard deviation of the measured currents should be less than or equal to 17.8% (one-half of the standard deviation calculated from the Horwitz function, 1/2 \( \text{RSD}_{\text{Hg}} \)). Under these conditions, all obtained \( I_p \) of mercury have satisfactory repeatability with RSD \( \leq 11.7% \) \((n = 4)\) (Figure 2). However, in order to achieve better repeatability with RSD < 10%, the concentration of Au(III) to be added to the solution must be \( \geq 0.2 \) mg/L.

3.3. DP-ASV Signal of Hg on Au–Cu Film Electrode

3.3.1. Effect of Au(III) and Cu(II) Concentrations. As seen in Figure 2, it is possible to increase the \( I_p \) and repeatability of mercury \( I_p \) by increasing \( C_{\text{Au(III)}} \) to form a gold film on the AuF/CPE. However, with the aim of reducing analysis costs, it is necessary to reduce the amount of Au(III) used during the analysis. Preliminary experiments indicated that, although stripping signal of Hg was not obtained on the copper film electrode (Figure 1), when adding a small amount of Cu(II) to a Hg(II) solution containing Au(III), the \( I_p \) of Hg increased. This shows the possibility to replace part of Au(III) in analyte solution by Cu(II) when creating a film electrode for Hg determination, thus reducing the cost of analysis as mentioned above.

The effect of \( C_{\text{Au(III)}} \) and \( C_{\text{Cu(II)}} \) on differential pulse anodic stripping currents of Hg.

| \( C_{\text{Au(III)}} \) (mg/L) | \( C_{\text{Cu(II)}} \) (mg/L) | \( I_p \) (\( \mu A \)) | RSD (%; \( n = 4) \) |
|--------------------------------|--------------------------------|-----------------|-----------------|
| 0                             | 0.20                          | -               | -               |
| 0.10                          | 0                             | 1.07            | 9.0             |
| 0.10                          | 0.05                          | 1.34            | 1.9             |
| 0.10                          | 0.10                          | 1.25            | 2.6             |
| 0.10                          | 0.20                          | 1.18            | 3.0             |
| 0.20                          | 0                             | 1.84            | 6.1             |
| 0.20                          | 0.05                          | 2.56            | 2.0             |
| 0.20                          | 0.10                          | 2.18            | 3.1             |
| 0.20                          | 0.20                          | 1.79            | 2.8             |
| 0.30                          | 0                             | 2.72            | 3.2             |

*No stripping peak of Hg appeared. Conditions: \( C_{\text{Hg(II)}} = 0.20 \) mg/L; \( C_{\text{HClO}_4} = 10^{-3} \) M; \( C_{\text{Au(III)}} = 0.1–0.5 \) mg/L; \( C_{\text{Cu(II)}} = 0.0–0.20 \) mg/L; other conditions as in Figure 1.

Experiment results presented in Table 1 show that adding Cu(II) to the Hg(II) analyte solution containing Au(III) causes an increase in the \( I_p \) of Hg. However, as the concentration of Cu(II) gradually increases, \( I_p \) tends to decrease.

![Figure 1: DP-ASV curves of 5 \( \mu \)g/L Hg(II) solutions containing 10⁻³ M HClO₄ and (1): without Cu(II); (2): 0.1 mg/L Cu(II) at CPE. Conditions: \( E_{\text{dep}} = -1100 \) mV; \( t_{\text{dep}} = 270 \) s; \( \omega = 2000 \) rpm; \( t_{\text{equal}} = 15 \) s; pulse amplitude \( (E_{\text{amplitude}}) = 70 \) mV; \( t_{\text{pulse}} = 40 \) ms; potential step \( (E_{\text{dep}}) = 6 \) mV; sweep rate \( (v) = 15 \) mV/s; potential range \( (E_{\text{range}}) = -100 \) mV to +1000 mV; \( E_{\text{clean}} = 800 \) mV; \( t_{\text{clean}} = 20 \) s.](image1)

![Figure 2: Influence of concentration of Au(III) on \( I_p \) of Hg. Conditions: error bars: standard deviation \( (n = 4) \); \( C_{\text{Hg(II)}} = 5 \) \( \mu \)g/L; \( C_{\text{HClO}_4} = 10^{-3} \) M; \( C_{\text{Au(III)}} = 0.1–0.5 \) mg/L. Other conditions as in Figure 1.](image2)
Table 2: Effect of acid types in electrolytic solutions on the $I_p$ of Hg at Au-CuF/CPE.

| Acid types | $10^{-3}$ M HCl | $10^{-3}$ M HNO$_3$ | $10^{-3}$ M HClO$_4$ |
|------------|-----------------|----------------------|----------------------|
| $I_p$ ($\mu$A) | 1.49            | 4.05                 | 4.29                 |
| RSD (%) ($n = 3$) | 1.2             | 6.9                  | 2.1                  |

Conditions: $C_{Au(III)} = 0.2$ mg/L; $C_{Cu(II)} = 0.05$ mg/L; other conditions as in Figure 1.

Table 3: Effect of HClO$_4$ concentration on the $I_p$ of Hg at Au-CuF/CPE.

| $C_{HClO_4}$ (M) | 0.0001 | 0.0005 | 0.001 | 0.005 | 0.01 | 0.05 |
|------------------|--------|--------|-------|-------|------|------|
| $I_p$ ($\mu$A)   | 2.52   | 3.55   | 4.10  | 4.43  | 4.43 | 4.30 |
| RSD (%) ($n = 3$) | 2.4    | 0.7    | 1.3   | 1.3   | 1.6  | 4.4  |

Conditions as in Table 2.

Table 4: Effect of deposition potential on the $I_p$ of Hg at Au-CuF/CPE.

| $E_{dep}$ (mV) | -600 | -700 | -800 | -900 | -1000 | -1100 |
|---------------|------|------|------|------|-------|-------|
| $I_p$ ($\mu$A) | 3.20 | 3.26 | 3.96 | 4.06 | 2.88  | 2.83  |
| RSD (%) ($n = 3$) | 6.0   | 7.6  | 0.7  | 6.3  | 4.9   | 6.3   |

Conditions: $C_{Hg(II)} = 5$ $\mu$g/L; $C_{HClO_4} = 0.005$ M; $C_{Au(III)} = 0.20$ mg/L; $C_{Cu(II)} = 0.05$ mg/L; $t_{dep} = 270$ s; other conditions as in Figure 1.

Table 5: Effect of deposition time on the $I_p$ of Hg at Au-CuF/CPE.

| $t_{dep}$ (s) | 160 | 170 | 180 | 190 | 200 | 210 | 220 | 230 |
|---------------|-----|-----|-----|-----|-----|-----|-----|-----|
| $I_p$ ($\mu$A) | 3.60 | 3.74 | 3.81 | 3.93 | 4.01 | 4.17 | 4.21 | 4.28 |
| RSD (%) ($n = 3$) | 6.8  | 3.9  | 0.7  | 1.5  | 0.4  | 0.9  | 1.2  | 0.8  |

Conditions: $C_{Hg(II)} = 5$ $\mu$g/L; $C_{HClO_4} = 0.005$ M; $C_{Au(III)} = 0.20$ mg/L; $C_{Cu(II)} = 0.05$ mg/L; $E_{dep} = -800$ mV; other conditions as in Figure 1.

Adding Au(III) and Cu(II) to concentrations of 0.20 and 0.05 mg/L, respectively, allows to gain stripping peak current of Hg not to be significantly different from $I_p$ obtained using an alone Au(III) dose of 0.30 mg/L but reduces the needed amount of Au(III) by 1/3. Therefore, $C_{Au(III)} = 0.20$ mg/L and $C_{Cu(II)} = 0.05$ mg/L are selected for further experiments.

When using Au-CuF/CPE electrode prepared by using an ex situ technique to record the DP-ASV signal of Hg(II) solution, the obtained stripping peak of Hg was ill-defined, low, and poorly reproducible compared when using an in situ electrode (Figure 3). This might be due to fewer electrochemically active sites formed on the surface of ex situ Au-CuF/CPE than on the in situ one. In addition, the number of active sites might also strongly fluctuate from the time of electrolyzing to the time of electrode transfer to the analyte solution for measurement.

3.3.2. Effect of Acid Types. The stripping voltammetry signals of mercury at Au-CuF/CPE are affected significantly by the supporting electrolytes, especially the type and concentration of acid. The 0.001 M solutions of HCl, HNO$_3$, and HClO$_4$ were used to study their effect on the DP-ASV signals of mercury (Table 2). The $I_p$ of mercury in the presence of HCl is lower than that in the presence of HNO$_3$ or HClO$_4$ with high RSD. This is possibly because Cl$^-$ can form complex with Au(III), causing the gold film to dissolve easily during the potential anodic scan. The microstructure of the electrode is not stable, and the $I_p$ changes [19]. Besides, Hg(II) can also form complex with Cl$^-$, and hence, the stripping potential of Hg(II) also decreases, and the stripping of Hg displaces negatively compared with the solution containing HNO$_3$ or HClO$_4$. The $I_p$ of Hg in the HClO$_4$ solution is higher and more stable than that in the HNO$_3$ solution. Therefore, HClO$_4$ is chosen for further experiments.

As shown in Table 3, when the concentration of HClO$_4$ increases from 0.0001 to 0.05 M, the stripping peak current of Hg on the Au-CuF/CPE has the highest value (4.43 $\mu$A) at $C_{HClO_4} = 0.005$ M and remains stable after this.
analytes with the ASV method, the deposition potential single-metal Au(0) and Cu(0) on the working electrode surface. When is reduced to Hg(0). Then, Hg(0) forms amalgams with step with a negative potential applied to the electrode, Hg(II)

\[ \text{Au(0) + Hg(II) \rightarrow Au-CuF/CPE amalgam} \]

Table 6: Influence of Fe(III), Ca(II), and Cu(II) on the \( I_p \) of Hg.

| Fe(III) | \( C_{Fe(III)} \) (mg/L) | \( I_p \) (μA) | RSD (%, \( n = 3 \)) | \( \Delta I_p \) (%) |
|---------|--------------------------|---------------|----------------------|-------------------|
|         | 0                        | 1.7           | 1.8                  | 1.9               |
|         | 2                        | 1.8           | 1.9                  | 2.0               |
|         | 3                        | 2.0           | 2.1                  | 2.1               |
|         | 4                        | 2.1           | 2.1                  | 2.1               |

| Cu(II) | \( C_{Cu(II)} \) (mg/L) | \( I_p \) (μA) | RSD (%, \( n = 3 \)) | \( \Delta I_p \) (%) |
|--------|-------------------------|---------------|----------------------|-------------------|
|        | 0.01                    | 1.2           | 1.1                  | 1.1               |
|        | 0.02                    | 1.1           | 1.1                  | 1.0               |
|        | 0.03                    | 1.0           | 1.0                  | 1.0               |
|        | 0.04                    | 1.0           | 1.0                  | 1.0               |
|        | 0.05                    | 1.0           | 1.0                  | 1.0               |

| Ca(II) | \( C_{Ca(II)} \) (mg/L) | \( I_p \) (μA) | RSD (%, \( n = 3 \)) | \( \Delta I_p \) (%) |
|--------|-------------------------|---------------|----------------------|-------------------|
|        | 0.7                     | 1.7           | 1.7                  | 1.8               |
|        | 2.2                     | 1.5           | 1.5                  | 1.8               |
|        | 3.7                     | 2.1           | 2.1                  | 2.1               |
|        | 5.8                     | 2.1           | 2.1                  | 2.1               |
|        | 0.7                     | 0.5           | 0.5                  | 0.9               |
|        | 23.5                    | 23.5          | 23.5                 | 23.5              |

Conditions: \( C_{Hg(II)} = 2 \mu g/L \); other conditions as in Figure 1.

concentration. Therefore, the \( C_{HClO_4} \) of 0.005 M was chosen for next experiments.

3.3.3. Effect of Deposition Potential. During the deposition step with a negative potential applied to the electrode, Hg(II) is reduced to Hg(0). Then, Hg(0) forms amalgams with Au(0) and Cu(0) on the working electrode surface. When single-metal film electrodes are used to determine the trace analytes with the ASV method, the deposition potential significantly affects the results of the analysis by affecting the microstructure of the metal film on the surface of the working electrode. The \( I_p \) of Hg(II) was recorded with \( E_{dep} \) changing from -600 to -1300 mV. On the Au-CuF/CPE electrode, \( I_p \) increases until the potential decreases to -900 mV, reaching a value of 4.06 μA with an RSD of 6.3%, then decreases significantly (Table 4). It is possible that at these negative potentials, H₂ air bubbles appear on the electrode surface, reducing the deposition efficiency. The -800 mV deposition potential was selected for further experiments because \( I_p \) measured at this potential (3.96 μA) does not differ significantly from the \( I_p \) value obtained at -900 mV (4.06 μA) but has a better repeatability (RSD = 0.7%).

3.3.4. Effect of Deposition Time. As the deposition time increases, the \( I_p \) of Hg increases slightly (Table 5). On the Au-CuF/CPE electrode, \( I_p \) increases gradually from 3.60 to 4.28 μA in the range of 170–230 s, with a fluctuation of RSD. As a compromise between reasonable analysis time and stripping peak signal, the deposition time of 180 s was selected as an appropriate deposition time for further applications.

3.4. Repeatability, Limit of Detection, and Linear Range. With the appropriate voltammetry conditions presented in Table 5, the 20-time repeated measurements of \( I_p \) of a 5 μg/L Hg(II) solution gained a good repeatability with RSD = 5.8% (<1/2 RSD of 17.8% at the analyte concentration level of 5 μg/L [18]).
that of Hg(II)/Hg0, or these cations may have the stripping potential close to that of Hg, causing the stripping potentials to overlap. The formation of intermetallic compounds may deform the stripping peak of Hg. The anions can form stable complexes or precipitation with Hg, affecting the preconcentration process. The surfactants can strongly adsorb on the surface of the working electrode, preventing the preconcentration and/or the dissolution of Hg. Therefore, it is necessary to study the influence of the interferents (commonly encountered in surface waters) on the determination of Hg.

The influence of the interfering ions/substances is assessed through the relative deviation between \( I_p^* \) in the presence of interference and without them \( (I_p^0) \) according to the following formula:

\[
\Delta I_p = \frac{I_p^* - I_p^0}{I_p^0} \times 100\%.
\]

When \(|\Delta I_p|\) is less than or equal to one-half of the relative standard deviation calculated from the Horwitz function \((1/2 \text{ RSD}_{\text{Hg}})\), the interfering effect is considered negligible. With \( C_{\text{Hg}[\text{II}]} = 2 \, \mu\text{g/L} \), the calculated 1/2 RSD_{\text{Hg}} is 20.4%.

3.5. Interference Study. In real river or lake water samples, there exist metal ions, such as Fe(III), Cu(II), and Ca(II); anions, such as \( \text{Cl}^- \), \( \text{SO}_4^{2-} \), and \( \text{PO}_4^{3-} \) (with a mg/L concentration); and surfactants. These interferents may have much a higher concentration than Hg(II) and may affect the \( I_p \) value of Hg and therefore influence the DP-ASV method with the Au-CuF/CP electrode.

The reasons for this interference may include the following: the redox potential of the interferent cations is close to that of Hg^{0}/Hg^{+}, or these cations may have the stripping potential close to that of Hg, causing the stripping potentials to overlap. The formation of intermetallic compounds may deform the stripping peak of Hg. The anions can form stable complexes or precipitation with Hg, affecting the preconcentration process. The surfactants can strongly adsorb on the surface of the working electrode, preventing the preconcentration and/or the dissolution of Hg. Therefore, it is necessary to study the influence of the interferents (commonly encountered in surface waters) on the determination of Hg.

The influence of the interfering ions/substances is assessed through the relative deviation between \( I_p^* \) in the presence of interference and without them \( (I_p^0) \) according to the following formula:

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\Delta I_p = \frac{I_p^* - I_p^0}{I_p^0} \times 100\%.
\]

When \(|\Delta I_p|\) is less than or equal to one-half of the relative standard deviation calculated from the Horwitz function \((1/2 \text{ RSD}_{\text{Hg}})\), the interfering effect is considered negligible. With \( C_{\text{Hg}[\text{II}]} = 2 \, \mu\text{g/L} \), the calculated 1/2 RSD_{\text{Hg}} is 20.4%.

Table 8: Anodic stripping voltammetry method for mercury determination.

| No. | Voltammetry | Electrode | Modifier | Deposition time (s) | Linearity (µg/L) | LOD (µg/L) | Real samples | Ref. |
|-----|-------------|-----------|----------|-------------------|-----------------|-------------|--------------|-----|
| 1   | ASV         | GC        | Submicrometer particulate Cu film | 300 | 10–100 | 0.1 | — | [12] |
| 2   | ASV         | GC        | Reduced graphene oxide/Au NPs nanocomposite | 600 | 0.2–30.15 | 0.12 | Tap water | [22] |
| 3   | DP–ASV      | Au        | —        | 120 | 0–50 | 0.05 | Tap water, pond water, wastewater | [23] |
| 4   | DP–ASV      | ITO*      | Au NPs   | 300 | 0.1–10 | 0.03 | Tap water, lake water, milk, soil sample | [24] |
| 5   | DP–ASV      | Carbon paste | KCdPb_{5}(PO_4)_3 lacunar apatite | 90 | 0.04–20 | 2.23 | Sea water, fish samples | [25] |
| 6   | DP–ASV      | BDD**     | —        | 30 | 2–10 | 2 | Power plant samples | [26] |
| 7   | DP–ASV      | BDD       | —        | 60 | 0.005–50 | 0.07 | Groundwater, soil samples | [27] |
| 8   | DP–ASV      | Carbon paste | Au NPs-bismuth | 200 | 1–10 | 0.28 | — | [28] |
| 9   | DP–ASV      | GC        | Au–Cu    | 250 | 1–5 | 0.09 | — | [17] |
| 10  | DP–ASV      | Carbon paste | Au–Cu | 180 | 1–5 | 0.13 | River water, groundwater | This study |

| *ITO: indium tin oxide; **BDD: boron-doped diamond. |
To confirm the applicability of the DP-ASV method using Au-CuF/CPE in practice, we first controlled its accuracy via the spike recovery (Rev), the recovery of a known addition, or spike, of analyte to a sample. To determine a spike recovery, a river water (Phuoc Son District, Quang Nam Province, Vietnam, named PS) was split into two portions, and a known amount of a standard spike was added to one portion. The concentration of Hg(II) was determined for both the spiked, unspiked portions, and the recovery of a known addition, or spike, of analyte to a sample was calculated as the following formula:

\[ \text{Rev} = \left( \frac{C_2 - C_1}{C_0} \right) \times 100 \]  

where \( C_0 \) (\( \mu g/L \)) is the concentration of Hg(II) added to the sample, \( C_1 \) (\( \mu g/L \)) is the concentration of Hg(II) in the unspiked portion, and \( C_2 \) (\( \mu g/L \)) is the concentration of Hg(II) in the spiked portion.

The recoveries at different standard spiked concentrations were within the expected values of 60-115% at 1-10 \( \mu g/L \) of the analyte (Table 9), issued by international organizations [18, 29].

### Table 10: Mercury content in natural water samples analyzed by DP-ASV using Au-CuF/CPE and CV-AAS.

| Sample | Type of sample | Location | \( C_{\text{Hg}} \pm SD \ (\mu g/L, \ n = 3) \) | DP-ASV | CV-AAS |
|--------|----------------|----------|-----------------------------------------------|--------|--------|
| HB     | Detention lake water spiked with 1.0 \( \mu g \) Hg/L | Quang Ngai City, Vietnam | 0.787 ± 0.151 | 0.802 ± 0.134 |
| HN     | Detention lake water spiked with 1.0 \( \mu g \) Hg/L | Quang Ngai City, Vietnam | 0.937 ± 0.265 | 0.836 ± 0.102 |
| PS     | River water | Phuoc Son District, Quang Nam Province, Vietnam | <LOD (NA) | <LOD (NA) |
| SRi    | River water | Son Ha District, Quang Ngai Province, Vietnam | <LOD (NA) | <LOD (NA) |
| SRi    | River water | Son Ha District, Quang Ngai Province, Vietnam | 0.195 ± 0.008 | (NA) |
| DM     | Hydropower plant reservoir | Phuoc Son District, Quang Nam Province, Vietnam | 0.384 ± 0.010 | (NA) |
| GK     | Underground water | Tam Ky City, Quang Nam Province, Vietnam | <LOD (NA) | (NA) |

(NA): not available.
The data on the Hg concentration in some water sources in Quang Nam Province and Quang Ngai Province, Vietnam, are presented in Table 10.

Using two-sided t-tests to evaluate the results of analysis of HB, HN using 2 methods shows that the measurement results using these two methods are not different significantly.

These quality control experiments indicate that the accuracy of the determination result of Hg(II) by using the DP-ASV method with in situ Au-CuF/CPE is reliable. Therefore, this method is suitable for the analysis of Hg(II) in natural water samples.

4. Conclusion

This paper presents the development of gold-copper film electrode formed in situ on the carbon paste substrate. The DP-ASV method developed with these electrodes has a relatively short deposition time and low limit of determination. The method is not significantly affected by the compounds that commonly exist in the water samples. It is possible to develop an analytical process to apply this method in practice.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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