

Research Article

Determination of Total Mercury in Solid Samples by Anodic Stripping Voltammetry

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The anodic stripping voltammetry (ASV) was investigated to determine total mercury in solid samples using a gold electrode. The mercury was deposited on the gold electrode in a preconcentration step. The oxidation peak of mercury was irreversible. The optimal conditions of the procedure were found to be as follows: 0.05 mol L⁻¹ HCl solution, deposition potential -0.5 V vs. Ag/AgCl/KCl, deposition time 40 s, and sweep rate 0.04 V s⁻¹. Under the optimal conditions, the peak current showed a linear dependence on Hg²⁺ concentration in the range from 0.01 to 0.1 mg l⁻¹. The detection limit and quantification limit were 4.28 μg L⁻¹ and 12.98 μg L⁻¹, respectively. The mean recovery and relative standard deviation were 91.2% and 2.4% (*n* = 9). The procedure was successfully applied for determining total mercury in samples collected from Hanoi light bulb warehouse—The Rang Dong Light Source and Vacuum Flask JSC. The results were compared with cold vapor atomic absorption spectrometry (CV-AAS).

1. Introduction

The high-level toxicity of mercury depends on its chemical forms such as the form of methylmercury has more toxicity than the form of elemental mercury [1–3]. When mercury enters the food chains, its concentration deposits and increases in the food change, affecting the life of many animals [4, 5]. In the past, mercury was used in several applications such as dentistry, industry, and mining. Unlike other heavy metals, Hg appearance is universal due to its unique physicochemical properties (volatility, long persistence in the atmosphere, solubility in water and lipids, and incorporation in organometallic compounds) and the possibility of transportation in atmosphere with deposition at considerable distances from the sources [6]. The Health Canada organizations warned their high level of contaminants in soil with the purpose of protecting human health and environmental quality according to various land

use types such as agricultural and commercial industry is 6.6 mg kg⁻¹ [7, 8]

The mercury concentrations in the nature environment are low due to the breakdown of minerals in rocks and soils caused by the wind and water [9]. However, the human activities (such as the mining and the combustion of fossil fuel and solid waste) release a large amount of mercury concentration in the environment [8, 10, 11].

About 54% of the global mercury emission from anthropogenic sources was contributed by Asian countries in 2000 [12]. In Vietnam, the pollution of mercury has become a serious problem due to many environmental incidents happened in the recent year. One of the most serious problem accidents happened in Vietnam is the burning of the Rang Dong Light Source and Vacuum Flask Joint Stock Company on August 28, 2019. The fire from the accident released about 15.2–27.2 kilograms of mercury into the environment. Therefore, the development of a method for

determining total mercury in the environmental sample is very necessary.

Many methods have been reported for the determination of mercury such as high chromatography-inductively coupled plasma mass spectrometry (HPLC/ICP-MS) [13, 14], gas chromatography-mass spectrometry (GC/MS) [2, 15], graphite furnace atomic adsorption spectrometry (GF-AAS) [5, 16, 17], cold vapor atomic absorption spectrometry (CV-AAS) [3, 9, 18, 19], cold vapor atomic fluorescence spectrometry (CV-AFS) [4, 20, 21], chemical vapor generation atomic emission spectrometry (CVG-AES) [22], UV-Vis spectrophotometric [23, 24], and anodic stripping voltammetry (ASV) [25–36]. Compared to the ASV methods, the HPLC-MS and GC-MS methods require complex sample preparations and the use of toxic organic solvents (e.g., methanol and acetonitrile), and the analytical is also more complex. The advantages of the anodic stripping voltammetry are no prior separation, high selectivity, low cost, and simplicity.

Several electrodes can be used to determine mercury by stripping voltammetry, for instance, glassy carbon electrodes, gold electrodes [25, 27, 31, 37], modified electrode [29, 35, 38–40], and screen-printed carbon electrodes [41]. The gold electrode has high conductivity and ductility. Moreover, the gold electrode exhibits a high affinity for mercury; hence, it improves selectivity of method. Therefore, the gold electrode was used widely to study the electrochemical behaviors and determine mercury in samples [26]. Depending on the analytical methods and types of sample, specific sample preparations are required such as using aqua regia combined with potassium permanganate solution [1], using mixture of strong acids, and using ultrasonication [42]. The solid samples, which were burned at very high temperature from the accident of the Rang Dong Light Source and Vacuum Flask Joint Stock Company, were collected.

In this research, we proposed a new, low cost, high sensitivity and selectivity analytical method for the determination of mercury in the solid samples applying the anodic stripping voltammetry combining with the gold electrode as the working electrode.

2. Materials and Methods

2.1. Reagents and Instrumentation. All chemicals were of analytical grade or higher quality.

All solutions were prepared with double distilled water (ddH₂O). All reagents were analytically pure. A stock solution of mercury (II) was 1000 ppm. The supporting electrolyte was 2 mol L⁻¹ HCl, 37% (Merck) HCl, 98% (Merck) H₂SO₄, and 68% (Merck) HNO₃.

All measurements for determination of mercury were done on the μ Autolab type III (Netherlands), interfaced to the electrode assembly 663 VA Metrohm (Switzerland), and controlled by software 757 VA. The system consists of a working gold electrode ($d=1$ mm; purchased from Metrohm), an AgCl/Ag/KCl reference electrode, a counter-electrode, a stirring glassy carbon rod, and high-purity nitrogen.

2.2. Analytical Procedure. A gold electrode was inserted into the cell, and then, 50.0 mL of the analytical solution containing 0.05 mol L⁻¹ HCl was added. Prior to the voltammograms measurement, the nitrogen flow was passed through the solution for the removal of oxygen. The differential pulse anodic stripping voltammetry was used to determine Hg²⁺. The accumulation step was carried out under potential of -0.5 V (vs. Ag/AgCl/KCl_s) for 40 seconds, while the analytical solution was being stirred. After that, the stirring was stopped for 5 s, and the differential pulse voltammograms were recorded from -0.5 to 0.7 V. All measurements were carried out at room temperature ($25 \pm 1^\circ\text{C}$).

2.3. Samples Preparation. The solid samples were collected from the Rang Dong Light Source and Vacuum Flask Joint Stock Company after the burning accidents on August 28, 2019. Stones, gravel, and light were removed the samples. Then, we weighed accurately using an analytical balance with uncertainty ± 0.0001 g. The amounts of samples (0.1–0.5 g) were transferred to the 50 mL beakers. A 10 mL of 37% (w/v) HCl acid was added to each sample. After that, the beakers were covered with a watch glass and boiled at 100°C in 60 min. After 60 mins, the sample was hot filtered using a $0.45 \mu\text{m}$ filter. The obtained solution was transferred into a 50.0 mL volumetric flask and made up to 50.0 mL with ddH₂O. The analytical procedure of measurement was described in Section 2.2.

The concentrations of Hg²⁺ in the solid samples were calculated by the following equation:

$$C \text{ (mg} \cdot \text{kg}^{-1}\text{)} = \frac{C_{\text{ob}} \text{ (mg} \cdot \text{L}^{-1}\text{)} \times k \times V \text{ (l)}}{a \text{ (kg)}}, \quad (1)$$

where C_{ob} is the concentration obtained in solution sample, V is the volume of solution sample, k is the dilution coefficient, and a is the mass of sample.

2.4. Method Evaluation. After optimizing experimental conditions and instrumental parameters, the suitable conditions were selected to determine mercury. The developed method was evaluated through linear range, limit of detection, limit of quantitation, precision, and recovery. The linearity calibration curve was built in standard solutions and spike solid samples from 10 to 100 ppb and 10 to 150 ppb, respectively.

The recovery was determined by spiking a known amount of total mercury in the solid sample. Then, this sample was prepared using the sample preparation described in Section 2.3. The concentration of mercury was determined by the standard addition method. The recovery was calculated according to the following equation:

$$\text{recovery (\%R)} = \frac{(C_f - C_i) \times 100\%}{C_{\text{ad}}}, \quad (2)$$

where C_i and C_f are the concentrations of mercury found in the sample before addition of standard solution and after addition of standard solution, respectively, and C_{ad} is the

concentration of standard mercury added in the solid sample.

2.5. Method Validation. To validate the analytical results of developed method, the same samples were sent to the standard laboratory of Vietnam Academy of Science and Technology. The cold vapor atomic absorption spectrometry (CV-AAS) was used to determine mercury content in solid samples. The samples were digested by the mixture of three acids HClO_4 , HNO_3 , and H_2SO_4 in 50 ml quartz volumetric flask. After 30 minutes, the samples were cooled down to the room temperature and reconstituted to 50.0 mL by H_2O . Automatic mercury analyzer model HG-21 has been used for determining mercury in samples.

To compare results of the anodic stripping voltammetry (AAS) and the cold vapor atomic absorption spectrometry (CV-AAS), we used the paired T -test in 1 tail for checking whether or not the significant error between them [43].

The paired t value was calculated:

$$t_{\text{cal}} = \frac{(\bar{d})\sqrt{n}}{S_d}, \quad (3)$$

in that \bar{d} is the average of the difference between the two results by the following formula:

$$\bar{d} = \frac{\sum_{i=1}^n d_i}{n}. \quad (4)$$

And S_d is the standard deviation of the difference and is calculated as follows:

$$S_d = \sqrt{\frac{\sum (d_i - \bar{d})^2}{n - 1}}. \quad (5)$$

3. Results and Discussion

3.1. Cyclic Voltammetry. Electrochemical properties of mercury(II) were investigated by cyclic voltammetry method and displayed in Figures 1–3. Figure 1 shows that the voltammograms of mercury(II) were not reversible caused by the i_{pa} to i_{pc} ratio smaller than 1 [44]. The peak current signal appeared in an oxidation zone, which means mercury (II) exhibits oxidative properties. The electrochemical reaction on the surface of working electrode was irreversible, and no reduction peak appeared on the cyclic voltammograms.

To investigate the accumulation behaviors of mercury on the surface of the gold electrode, the cyclic voltammetry was recorded with different deposition time conditions, specifically 0, 30, and 60 seconds at the same deposition potential of -0.5 V of $0.1 \text{ mg l}^{-1} \text{ Hg}^{2+}$ in $0.05 \text{ mol. L}^{-1} \text{ HCl}$ solution. Figure 2 shows that the peak current of mercury depended on deposition time. When deposition time increased, the peak current increased, which indicated that mercury had deposition on the electrode surface.

The effect of scan rate on the oxidation peak current (I_{pa}) of $0.1 \text{ mg l}^{-1} \text{ Hg}^{2+}$ in $0.05 \text{ mol l}^{-1} \text{ HCl}$ solution using gold electrode was investigated in the range from 10 to 1000 mV s^{-1} . Figure 3 indicates that the relationship between

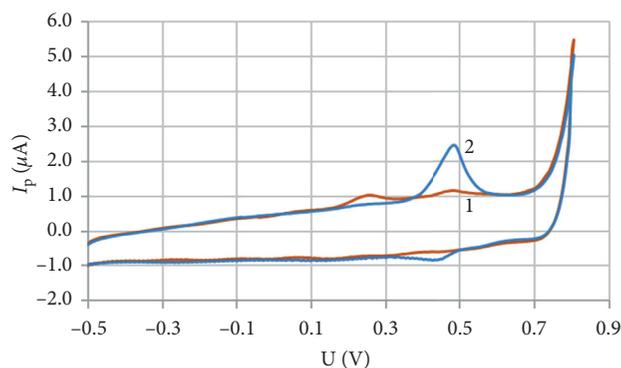


FIGURE 1: Cyclic voltammograms at sweep rate 0.1 V.s^{-1} , voltage step 6 mV , start potential -0.5 V , and end potential 0.8 V : (1) blank ($\text{HCl } 0.05 \text{ mol l}^{-1}$); (2) $0.1 \text{ mg l}^{-1} \text{ Hg}^{2+}$ in $0.05 \text{ mol l}^{-1} \text{ HCl}$.

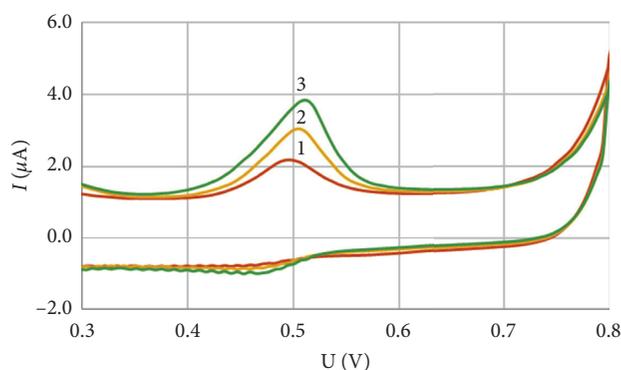


FIGURE 2: Cyclic voltammograms of $0.1 \text{ mg l}^{-1} \text{ Hg}^{2+}$ in $\text{HCl } 0.05 \text{ mol l}^{-1}$, deposition potential -0.5 V , sweep rate 0.1 V s^{-1} , and voltage step 6 mV : (1) deposition time 0 s ; (2) deposition time 30 s ; (3) deposition time 60 s .

the oxidation peak current and sweep rate in cyclic voltammetry was linearly dependent according to the equation $\log I_p = 0.85 \log \nu + 4.94$, $R^2 = 0.997$ ($n = 14$). Theoretically, the slope value of 1.0 suggests the electrochemical reaction occurred on the surface of working electrode, while the value of 0.5 indicated that the current is controlled by semi-infinite diffusion reaction kind in the solution [45]. By fitting the plot of $\log(i)$ as a function of $\log(\nu)$, the slope value for mercury oxidation peak was 0.85, which indicated that mercury (II) possessed a strong accumulation character onto the gold electrode surface. Therefore, the concentration of mercury was determined by differential pulse anodic stripping voltammetry.

3.2. Differential Pulse Anodic Stripping Voltammetry

3.2.1. Choice of Supporting Electrolytes. A high supporting electrolyte concentration is used to minimize the effects of migration to the electrode surface and to reduce the cell resistance which decreases the IR drop. So, the supporting electrolyte is very important factor in voltammetry. To optimize the best medium, some electrolytes such as nitric

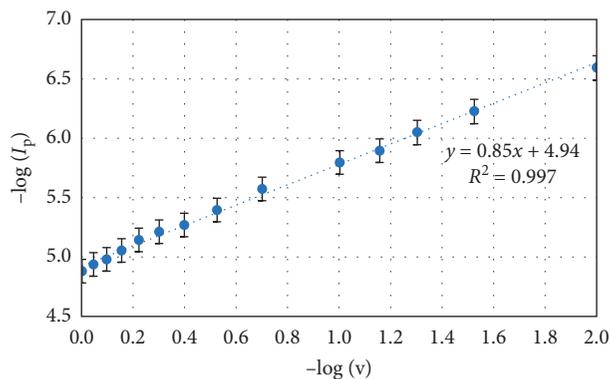


FIGURE 3: Cyclic voltammometry current ($\log I_p$) vs. $\log U$ plot for 0.1 mg L^{-1} mercury, deposition potential -0.5 V , deposition time 30 s , and scan rate from 10 mV s^{-1} to 1000 mV s^{-1} .

acid, hydrochloric acid, and sulfuric acid were added as measurement solution.

The voltammograms of the acids with 0.2 ppm of Hg are shown in Figure 4. The results indicated that presence of hydrochloric acid was essential to obtain a good peak current, so HCl solution was chosen to determine Hg^{2+} .

3.2.2. Effect of Hydrochloric Acid Concentration. The effect of HCl concentration on the signal of Hg^{2+} was investigated with the following conditions: the Hg^{2+} condition 0.1 mg l^{-1} , the sweep rate of 0.04 V s^{-1} , the pulse amplitude 0.05 V , and the pulse time 0.04 s . The results are presented in Figure 5.

Figure 5 shows that the HCl concentration affected the current peak of mercury. When HCl concentration increased from 0.01 to 0.05 mol l^{-1} , the peak current of mercury also increased. However, the peak current did not increase in the concentration range of 0.05 – 0.15 mol l^{-1} . When HCl concentration was higher than 0.15 mol l^{-1} , the mercury signal was decreased, which may be caused by the formation of Hg^{2+} complex with the excess chloride ions (Cl^-). Therefore, the concentration of 0.05 mol l^{-1} HCl was chosen for all following experiments for determination of mercury.

3.2.3. Effect of the Anodic Stripping Voltammetry Parameters.

The sensitivity of the anodic stripping voltammetry depends on both the deposition time and deposition potential. The dependence of the stripping peak current on the deposition potential was also investigated in the range from -0.9 V to 0.8 V for 0.05 mg l^{-1} mercury after preconcentration in 30 s . Figure 6 shows that the peak current was practically depended on the deposition potential. The highest value of peak current could be obtained at a deposition potential of -0.5 V . After that, the value of peak current decreased when deposition potential increased from -0.4 V to $+0.3 \text{ V}$. So, the deposition potential of -0.5 V was chosen for the rest of measurements.

Figure 7 indicates that the oxidation peak current increased when deposition time increased from 0 s to 80 s . After that, the oxidation peak current became independent

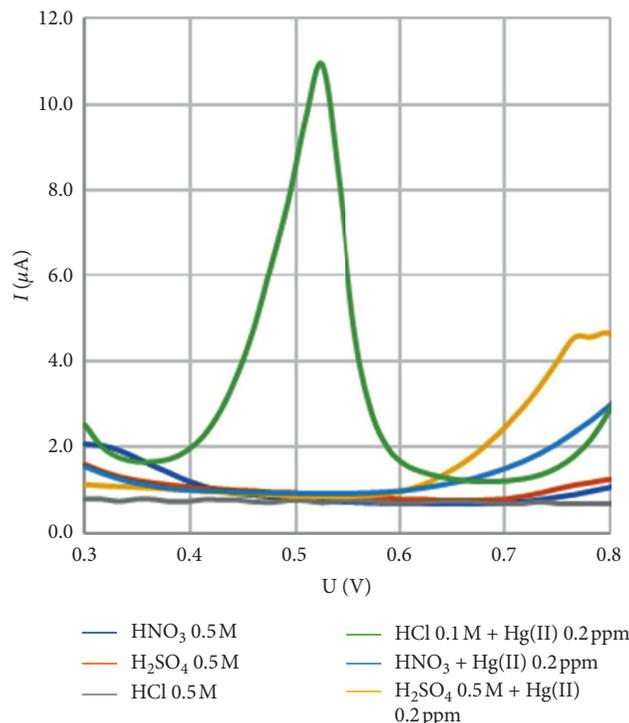


FIGURE 4: Differential pulse anodic stripping voltammograms of 0.5 mol l^{-1} HCl , HNO_3 , and H_2SO_4 and 0.2 mg l^{-1} Hg^{2+} in 0.5 mol l^{-1} HCl , HNO_3 , and H_2SO_4 , sweep rate 0.04 V s^{-1} , pulse amplitude 0.05 V , and pulse time 0.04 s .

with the deposition time, which indicated that the gold electrode surface was completely covered. Therefore, 40 seconds deposition potential was chosen for depositing 0.05 mg l^{-1} Hg^{2+} on the surface of working electrode.

In the anodic stripping voltammetry using differential pulse technique, the sweep rate affected the peak current. A well-defined peak current was obtained with 0.04 V s^{-1} of the sweep rate.

Accordingly, the optimal differential pulse parameters for the determination of Hg^{2+} were established as voltage step 4 mV , voltage step time 100 ms , sweep rate 40 mV s^{-1} , pulse amplitude 50 mV , and pulse time 40 ms . Linear calibration graphs for mercury were obtained from 0.01 mg l^{-1} to 0.1 mg l^{-1} with regression equation $i_{\text{pa}} (\mu\text{A}) = (0.0017 \pm 0.1601) + (0.0446 \pm 0.0026) \times C_x (\mu\text{g l}^{-1})$ and correlation coefficient 0.999 .

3.2.4. Validation of Method. The detection limit (LOD) and quantitation limit (LOQ) were calculated from the linearity calibration curves as $k \times \sigma/S$ [46] where $k = 3$ for LOD and 10 for LOQ, where σ stands for standard deviation and S is the slope of the calibration curve. The detection limit and quantification limit of mercury were found to be $4.28 \mu\text{g l}^{-1}$ and $12.97 \mu\text{g l}^{-1}$, respectively.

Precision was determined by eleven successive measurements of solution containing $50 \mu\text{g l}^{-1}$ Hg^{2+} in 0.05 mol l^{-1} HCl solution with deposition time of 40 s at deposition potential -0.5 V . The relative standard deviation (RSD) was 3.07% ($n = 11$). The results showed that the RSD

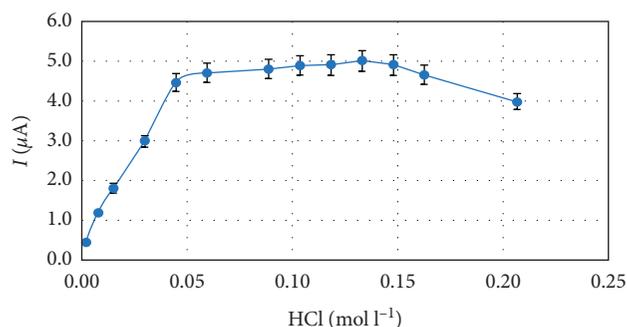


FIGURE 5: Influence of HCl concentration on the I_p for $0.1 \text{ mg L}^{-1} \text{ Hg}^{2+}$, sweep rate 0.04 V s^{-1} , pulse amplitude 0.05 V , and pulse time 0.04 s .

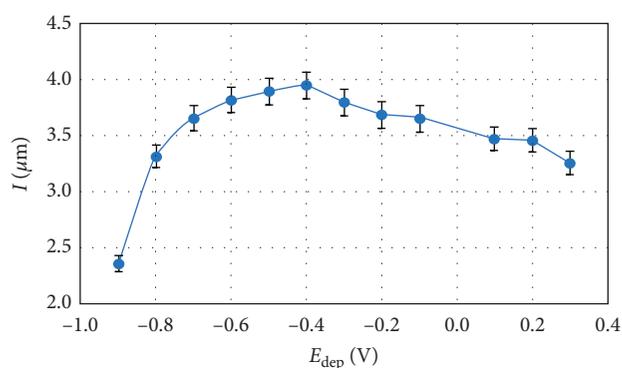


FIGURE 6: Effect of deposition potential (E_{dep}) on the anodic stripping peak current of $0.05 \text{ mg L}^{-1} \text{ Hg}^{2+}$ in $0.05 \text{ mol L}^{-1} \text{ HCl}$, $t_{\text{dep}} = 30 \text{ s}$, and sweep rate 0.04 V s^{-1} .

(%) was smaller than 5%. Therefore, the proposed analytical method has been good repeatability.

To evaluate the precision of the method before we applied to determine mercury in solid samples, two levels of concentration $50 \mu\text{g L}^{-1}$ and $100 \mu\text{g L}^{-1}$ of mercury were added into the solid sample and were analyzed repeatedly nine independent times. The mean recoveries based on nine replicate measurements were found to be $90.51 \pm 1.06\%$ and $91.53 \pm 0.91\%$. The relative standard deviation (RSD) was 2.49% and 2.42%, respectively ($n=9$). This level of precision was suitable to determine mercury in solid samples at the Rang Dong Light Source and Vacuum Flask Joint Stock Company after burning.

3.2.5. Application. The proposed procedure was successfully applied to determine mercury in solid samples. The quantitative determination of different concentrations of mercury in a spiked solid sample was carried out by using the proposed anodic stripping voltammetry procedure (Figure 8).

The variation in i_p versus mercury concentration C was represented by the straight-line equation $i_p (\mu\text{A}) = (0.1863 \pm 0.1302) + (0.0324 \pm 0.0015) \times C (\mu\text{g L}^{-1})$ (correlation coefficient 0.999 and $n=5$). The limits of detection

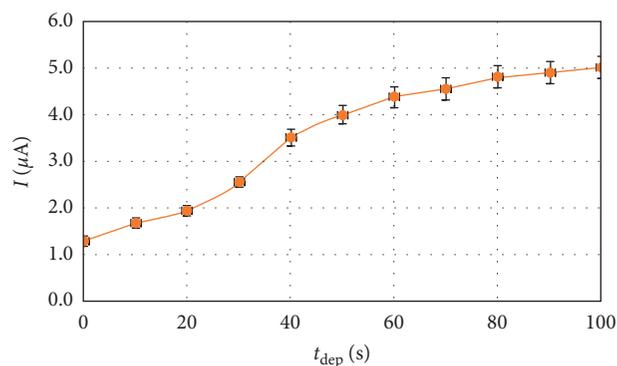


FIGURE 7: Effect of deposition time (t_{dep}) on the anodic stripping peak current of $0.05 \text{ mg L}^{-1} \text{ Hg}^{2+}$ in $0.05 \text{ mol L}^{-1} \text{ HCl}$, $E_{\text{dep}} = -0.5 \text{ V}$, and sweep rate 0.04 V s^{-1} .

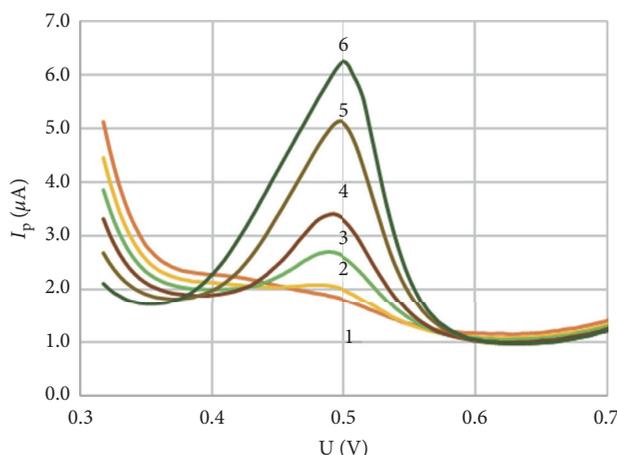


FIGURE 8: Anodic stripping differential pulse voltammograms for increased concentrations of mercury spiked in solid samples: (1) blank; (2) $10 \mu\text{g L}^{-1}$; (3) $30 \mu\text{g L}^{-1}$; (4) $50 \mu\text{g L}^{-1}$; (5) $100 \mu\text{g L}^{-1}$; (6) $150 \mu\text{g L}^{-1}$; $E_{\text{dep}} = -0.5 \text{ V}$, $t_{\text{dep}} = 40 \text{ s}$, sweep rate 40 mV s^{-1} , pulse amplitude 50 mV , pulse time 40 ms , and $0.05 \text{ mol L}^{-1} \text{ HCl}$.

(LOD) and quantitation (LOQ) of mercury in solid samples were found to be $5.57 \mu\text{g L}^{-1}$ and $16.88 \mu\text{g L}^{-1}$, respectively.

The accuracy of the method was verified by using the spiked solid samples. The mean recovery was found to be range from $89.8\% \pm 1.09$ to $92.6\% \pm 1.38$ ($n=9$ replicate measurements). The proposed method was applied to determine total mercury in solid samples collected at an accidental area. The results indicated that mercury was found in all samples collected from Hanoi light bulb warehouse. The highest concentration of mercury was $182.51 \text{ mg kg}^{-1}$. According to the standard of Canadian Health Organization, the allowable Hg^{2+} content in the soil is 6.6 mg kg^{-1} . The results showed that the concentration of total mercury in the six solid samples collected at the accidental area was higher than the permitted standard of health organization (Table 1). Therefore, we received that each industrial activity has potential risks for the environment.

To validate, the results obtained by the proposed ASV method was compared with those obtained by the CV-AAS

TABLE 1: Determination of mercury in solid samples by ASV and CV-AAS methods.

Number	Sample	ASV (mg kg ⁻¹)	CV-AAS (mg kg ⁻¹)	<i>d</i>
1	CR03	92.42	97.18	4.75
2	CR23	182.51	186.82	4.31
3	CR25	70.02	88.49	18.47
4	CR26	18.30	21.87	3.57
5	CR27	29.23	29.32	0.09
6	CR30	6.45	6.53	0.08
7	CR31	3.13	2.53	-0.60
8	CR33	31.82	32.15	0.32
9	CR34	2.76	0.76	-2.00
		\bar{d}		3.22
		S_d		6.19
		Paired <i>t</i> value		1.56

method. The results obtained by anodic stripping voltammetry (ASV) and the cold vapor atomic absorption spectrometry (CV-AAS) are summarized in Table 1.

We find that $t_{\text{calculated}}$ (1.56) is less than t_{table} (1.86) listed in Table 1 for 95% confidence and 8 degrees of freedom. There is more than a 5% chance that the two sets of results lie “within experimental error” of each other, so we conclude that the results are not significantly different. However, the ASV has highly sensitive, selective, fast, easy to use, low cost, and less expensive equipment. So, the anodic stripping voltammetry can apply to determine total mercury in the solid sample.

The proposed method was successfully applied to determine Hg²⁺ content in surface water samples collected from To Lich River without sample preparation. The analytical procedure of measurement was the same as in Section 2.2, but deposition time was 300 s. The Hg²⁺ content was found in 5 samples collected from To Lich River near Trung Hoa Bridge in May 2020. The Hg²⁺ content in samples was determined by 1 μg L⁻¹ Hg²⁺ addition standard method. The results obtained for the surface water samples are below the limit values for mercury. The average Hg²⁺ content in surface water samples was 0.67 μg L⁻¹. The results could confirm that the anodic stripping voltammetry can determine the Hg²⁺ content in water with increasing deposition time.

4. Conclusion

The anodic stripping differential pulse voltammetry was developed for the determination of total mercury in solid samples. The electrochemical behaviors of mercury were an irreversible process. The mercury was deposited on the surface of the gold electrode. With the optimum conditions, the proposed method has high selectivity, sensitivity, precision, accuracy, and well repeatability, with high recoveries from 89.8% to 92.6%. The proposed method successfully applied to the fast determination of mercury in solid samples collected from Hanoi light bulb warehouse—The Rang Dong Light Source and Vacuum Flask JSC. The results are in good agreement with cold vapor atomic absorption spectrometry.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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