Research Article

Determination of Chromium in Natural Water by Adsorptive Stripping Voltammetry Using In Situ Bismuth Film Electrode

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Received 2 August 2019; Revised 7 January 2020; Accepted 10 April 2020; Published 14 May 2020

Academic Editor: Evelyn O. Talbott

Development of adsorptive stripping voltammetry (AdSV) combined with in situ prepared bismuth film electrode (in situ BiFE) on glassy carbon disk surface using diethylenetriamine pentaacetic acid (DTPA) as a complexing agent and NO₃⁻ as a catalyst to determine the trace amount of chromium (VI) is demonstrated. According to this method, in the preconcentration step at E_{dep} = −800 mV, the bismuth film is coated on the surface of glassy carbon electrodes simultaneously with the adsorption of complexes Cr(III)-DTPA. In addition to the influencing factors, the stripping voltammetry performance factors such as deposition potential, deposition time, equilibration time, cleaning potential, cleaning time, and technical parameters of differential pulse and square wave voltammetries have been investigated, and the influence of Cr(III), Co(II), Ni(II), Ca(II), Fe(III), SO₄²⁻, Cl⁻, and Triton X has also been investigated. This method gained good repeatability with RSD < 4% (n = 9) for the differential pulse adsorptive stripping voltammetry (DP-AdSV) and RSD < 3% (n = 7) for the square wave adsorptive stripping voltammetry (Sqw-AdSV), and low limit of detection: LOD = 12.10⁻⁹ M = 0.6 ppb (at a deposition potential (E_{dep}) of −800 mV and the deposition time (t_{dep}) of 50 s) and LOD = 2.10⁻⁹ M = 0.1 ppb (at E_{dep} = −800 mV and t_{dep} = 160 s) for the DP-AdSV and SqW-AdSV, respectively. This method has been successfully applied to analyze chromium in natural water.

1. Introduction

In the natural environment, chromium exists in two thermodynamically stable states, Cr(VI) and Cr(III). Its toxicity depends on the level of oxidation; Cr(VI) is the causative agent of cancer through the airways and toxic to humans and other mammals, while Cr(III) at trace levels provides the body with essential minerals. The sources of chromium emissions into the environment are electroplating, metallurgical, dye processing, tanning, minerals, and refractory materials [1, 2]. The form of chromium does not only determine its ecological impact but also determines its movement and variation in the environment. Studies related to the transformation of Cr(VI), the distribution of Cr(III) between inorganic and organic compounds, and the treatment of chromium-contaminated environment are increasingly being considered [3, 4].

There are several sensitive methods for determining chromium such as atomic absorption spectrometry [5, 6], plasma emission spectrometry [7, 8], and capillary gas chromatography [9]. These methods, while highly sensitive, only reach the ppb size detection limit and often require preenrichment and extraction stages, which can lead to sample contamination, complicate processes, and increase the cost of analysis, and therefore, it will be difficult to require frequent and mass analysis of samples in the environment. To overcome these difficulties, in recent years, analysts have successfully applied the AdSV method. This method allows direct determination (i.e., no need to extract or evaporate the sample) of the amount of traces, even super
chromium traces in different objects, and achieves very low LOD, size $< 10^{-9} - 10^{-12}$ M [10–20].

Another problem raised was the working electrode used in the AdSV method. Currently, most studies on the AdSV method use hanging mercury drop electrodes (HMDEs) [21–34], or static mercury drop electrodes (SMDE) [19, 35] which are expensive and very difficult to fabricate. Research on the use of mercury film electrode (MFE) and bismuth film electrode on glassy carbon disk surface (BiFE), which are less expensive and easier to fabricate, and environmentally friendly BiFE has been improved.

AdSV has been applied in combination with different types of electrodes and stripping voltammetry signaling techniques, and many authors have been successful in determining the amount of traces and super chromium traces in complex objects. Most studies use HMDE electrodes, some use MFE electrodes, and there are also many ex situ BiFE electrodes [10, 11, 14, 16, 17, 36] and gold film electrodes (AuFE) [13, 15, 37–39], and the later modified electrodes [20, 36, 40–44] are applied more for chromium analysis in complex objects. The complex ligands used are DTPA [1, 21, 22, 25, 26, 28, 32, 35, 45], triethylenetetramine hexaacetic acid (TTHA) [19, 29, 31, 37], diphenylcarbazide (DPCB) [23, 29], pyrocatechol violet [24, 30], pyrogallol [34], rubeanic acid [33], neo TT [40], and quercetin [20], and the common base ingredients are CH$_3$COONa, acetate buffer (CH$_3$COOH/CH$_3$COONa), and CH$_3$COONa/NaNO$_3$; all studies analyzed chromium in river water, seawater, groundwater, tea water, and wastewater, and almost no works have analyzed chromium in sediments by the adsorptive stripping voltammetry method and no author has used in situ BiFE to analyze chromium in environmental objects. Overall, studies have achieved very low detection limits from $10^{-10}$ to $10^{-15}$ M (or from 0.05 ppb to 0.005 ppb). Table 1 shows the summary of published studies on chromium determination by the AdSV method.

When analyzing Cr(VI) by the AdSV method, Yong et al. [10] and Lin et al. [11] proposed the adsorption mechanism as follows.

The first stage of the adsorptive stripping voltammetry method is the movement of Cr(VI) in the solution to the electrode surface and is reduced by the following reaction.

$$\text{Cr(VI)} + 3e^- \rightarrow \text{Cr(III)}; \quad E_{1/2} = -0.2 \text{ V}$$

in comparison with 3 M Ag/AgCl/KCl electrode; in the presence of DTPA ions on the interface between the electrode membrane and the solution, Cr(III) ions form complexes quickly and adsorbed onto the electrode surface. The main nature of this complex is unknown, and some authors [21, 46] said that this complex exists mainly as Cr(III)-DTPA$^{2-}$ and a little in Cr(III)-HDTPA$^{-}$, or Khan [47] suggested that the complex of Cr(III) with DTPA exists as [Cr(III) (H$_2$O)$_2$HY$^-$], [Cr(III)-DTPA]$^{2-}$, and so on.

After complex adsorption, potential scan was conducted from $-0.9 \text{ V}$ to $-1.35 \text{ V}$ [10], or from $-0.8 \text{ V}$ to $-1.4 \text{ V}$ [11]; as a result of this process, the Cr(III)-DTPA complex is reduced to the Cr(II)-DTPA complex [10, 11]:

$$\text{Cr(III)} \rightarrow \text{DTPA} + e^- \rightarrow \text{Cr(II)} \rightarrow \text{DTPA} \quad (1)$$

The signal recorded with this reduction is at $E_{1/2} = -1.15 \text{ V}$ [10, 11] and at $E_{1/2} = -1.1 \text{ V}$ in comparison with 3 M Ag/AgCl/KCl electrode.

The role of NO$_3^-$ ions is to oxidize Cr(II)-DTPA complexes into Cr(III)-DTPA complexes.

Thanks to the oxidation of NO$_3^-$, the peak is higher and the sensitivity of the method is increased.

$$\text{Cr(II)} \rightarrow \text{DTPA} \rightarrow \text{NO}_3^- \rightarrow \text{Cr(III)} \rightarrow \text{DTPA} \quad (2)$$

In order to contribute to the development of the AdSV method, we have conducted several studies to determine chromium by the AdSV method using mercury film electrodes, ex situ bismuth film electrode, and in situ bismuth film electrode. In this paper, we present the results of chromium determination by the AdSV method using in situ bismuth film electrode (in situ BiFE) in the presence of DTPA as a complexing agent and ion NO$_3^-$ as a catalyst. Literature survey revealed that in situ BiFE has never been used for chromium determination by the adsorptive stripping voltammetry.

2. Experimental

2.1. Apparatus and Reagents. Square wave stripping voltammetric measurements were conducted on Electrochemical Analyzer 797 VA Computrace (Metrohm, Switzerland) accompanied with three electrodes. These electrodes were inserted into the 80 ml capacity electrochemical cell. The working electrode was a glassy carbon rotating disk electrode with $d = 2.8 \pm 0.1 \text{ mm}$; the reference electrode was a 3 M Ag/AgCl/ KCl electrode and the auxiliary electrode was a platinum wire. All measurements were carried out at 25 $\pm 1^\circ \text{C}$.

DTPA (diethylenetriamine pentaacetic acid) is used as a complexing agent for chromium. 50 $\times 10^{-3}$ M DTPA solution was prepared by dissolving $4.916 \text{ g}$ of DTPA in double-distilled water and then adding 25% aqueous ammonia solution until the pH reaches 6.0.

0.2 M Cr(VI) stock solution was prepared by weighing 7.35 g of K$_2$Cr$_2$O$_7$ (Merck, purity of 95–98%), dissolving, and making it up to 250 ml with double-distilled water. Cr(VI) working solutions such as Cr(VI) $10^{-6}$ M and Cr(VI) $10^{-7}$ M are diluted daily from this stock solution.

0.48 $\times 10^{-3}$ M Bi(III) working solution was prepared from 4.8 $\times 10^{-3}$ M Bi(III) (the type used for analyzing atomic absorption spectrometry from Merck).

Acetate buffer (pH = 6) was prepared from NaCH$_3$COO (Merck, purity of 95–98%) and CH$_3$COOH (Merck, purity 97%). 2.5 M NaNO$_3$ solution was prepared from NaNO$_3$ (Merck, purity of 95–98%).

Other metal ionic solutions such as Co(II), Ni(II), Zn(II), Cr(III), Fe(III), and Ca(II) are from the corresponding 1000 mg/l stock solution (the type used for analyzing atomic absorption spectrometry from Merck). Triton X-100 working solution was prepared from Triton X-100 (Merck).
| No. | Ligands | Background solution | Working electrode | Measurement techniques | LOD (pbb) | Analytical object | Determined form | Time of publication | References |
|-----|---------|---------------------|------------------|----------------------|----------|------------------|-----------------|---------------------|------------|
| 1   | DTPA    | CH₃COONH₄, NaNO₃ (pH = 5.2) | HMDE             | DP-AdSV             | 1.2      | Fake template    | Total chromium  | 1987                | [21]       |
| 2   | Diphenylcarbazide | H₂SO₄ 0.1 M | GE               | LSV                   | 0.05     | Fake template    | Cr(VI)          | 1988                | [29]       |
| 3   | TTHA    | CH₃COONa, NaNO₃ (pH = 5.5) | HMDE             | DP-CSV               | 1.04     | Fake template    | Cr(VI)          | 1988                | [29]       |
| 4   | TTHA    | CH₃COONa, NaNO₃ (pH = 5.5) | HMDE             | SqW-AV               | 0.02     | Fake template    | Cr(VI)          | 1988                | [29]       |
| 5   | DTPA    | KH₂PO₄, Na₂HPO₄ (pH = 6-7) | HMDE             | DP-CSV               | 0.01     | Fake template    | Groundwater     | 1990                | [32]       |
| 6   | Diphenylcarbazide | H₂SO₄ 0.3 M | HMDE             | DP-AdSV              | 0.02     | Groundwater      | Cr(VI)          | 1992                | [23]       |
| 7   | DTPA    | Acetate buffer (pH 5.2) | HMDE             | SqW-AdSV             | 0.05     | Seawater         | Cr(VI), total chromium | 1992        | [45]       |
| 8   | DTPA    | NaNO₃ 0.5 M, MES (morpholinoethanesulfonic acid) (pH 6.1) | HMDE             | DP-AdSV             | 0.62     | River water, tap water | Total chromium | 2000                | [28]       |
| 9   | DTPA    | NaNO₃, acetate buffer (pH 5.7) | HMDE             | DP-AdSV             | Cr(VI): 0.005 Cr(III): 0.52 | River water, lake water, sewer water | Cr(VI), activated Cr(III), total chromium | 2001        | [1]        |
| 10  | TTHA 0.1 M (triethylenetetraminhexaacetic acid) | | SMDE             | SqW-AdSV             | 0.52     | Leaf             | Cr(VI)          | 2003                | [19]       |
| 11  | DTPA    | Acetate buffer (pH 6), KNO₃ 0.25 M | HMDE             | DP-AdSV             | 0.004    | Wastewater       | Cr(VI), total chromium | 2004        | [22]       |
| 12  | Rubeanic acid (dithiooxamide) | Acetate buffer (pH 6), KNO₃ 0.20 M | HMDE             | DP-AdSV             | 1976     | River water, seawater, sewage, vinegar | Cr(VI) | 2012        | [33]       |
| 13  | DTPA    | Acetate buffer (pH 6) NaNO₃ | HMDE             | AdSV                 | 18.2     | Human urine      | Cr(VI) | 2005        | [26]       |
| 14  | TTHA 0.2 M | NaCH₃COO 0.1 M, NaNO₃ 5 M (pH 6.2) | HMDE             | CV-AdSV             | 0.3      | Human urine      | Cr(VI)          | 1997                | [31]       |
| 15  | DTPA    | NaCH₃COO 0.01 M, NaNO₃ 0.5 M (pH 8.5) | SMDE             | SqW-AdSV             | 0.05     | River water, tap water | Cr(VI) | 1999        | [35]       |
| 16  | DTPA    | NaCH₃COO 0.15 M, NaNO₃ 0.7 M (pH 6) | HMDE             | SqW-AdSV             | 0.05     | Cement           | Cr(VI) | 2011        | [25]       |
| 17  | Pyrogallol red | 0.4 M acetate buffer (pH 4.5) | HMDE             | SqW-AdSV             | 0.05     | Seawater         | Cr(VI), Cr(III), total chromium | 2012        | [34]       |
| 18  | DTPA    | NaCH₃COO 0.2 M (pH 6.2) | HMDE             | DP-AdSV             | 1.04     | Electroplating waste water | Cr(VI) | 2004        | [27]       |
| 19  | Pyrocatechol violet | Acetate buffer | HMDE             | DP-AdSV             | 0.15     | Electroplating waste water | Cr(VI) | 1997        | [24]       |
| 20  | Pyrocatechol violet | 0.1 M acetate buffer (pH 6) | HMDE             | DP-AdSV             | 0.05     | Electroplating waste water | Cr(VI) | 2004        | [27]       |

Table 1: Summary of published works on stripping voltammetry method for chromium determination.
| No. | Ligands          | Background solution                  | Working electrode         | Measurement techniques | LOD (pbb) | Analytical object                  | Determined form | Time of publication | References |
|-----|------------------|--------------------------------------|---------------------------|------------------------|-----------|------------------------------------|-----------------|---------------------|------------|
| 21  | Cupferron 0.01 M | PIPES 0.2 M (pH = 7)                 | BiFE ex situ              | SqW-AdSV               | 0.1       | Laboratory, cigarettes, soil sample| Total chromium  | 2004                | [14]       |
| 22  | DTPA 5 mM        | Acetate 0.1 M (pH = 6.0)             | BiFE ex situ              | SqW-AdSV               | 0.015     | River water                        | Total chromium  | 2005                | [11]       |
| 23  | DTPA 5 mM        | NaOAc 0.1 M (pH = 6.0)               | BiFE ex situ              | SqW-AdSV               | 0.015     | Blood sample                       | Total chromium  | 2006                | [10]       |
| 24  | DTPA 5 mM        | Acetate 0.1 M (pH = 6.0)             | BiFE ex situ              | SqW-AdSV               | 0.017 (Cr VI); 0.022 (Cr total) | River water                  | Cr(VI); Cr(III) | 2010                | [16]       |
| 25  | PAR (4-(2-pyridylazo) resorcinol) | CH₃COOH–CH₂COONa, trisodium citrate | BiFE ex situ              | SqW-AdSV               | 0.01      | Tap water, lake water, soil sample | Total chromium  | 2013                | [17]       |
| 26  | DTPA             | CH₃COONH₄, NaNO₃ (pH = 5.2)          | Bi film wrapped single walled carbon nanotubes | DP-AdSV               | 0.12. 10⁻³ | Fake template                     | Total chromium  | 2013                | [18]       |
| 27  | DTPA 0.01 M      | 0.1 M acetate buffer (pH = 6.0)     | Hg (Ag)FE                 | DP-AdSV               | 0.004     | Natural water, drinking water     | Cr(VI)          | 2006                | [12]       |
| 28  | TTHA             | CH₃COONa, NaNO₃ (pH = 5.5)           | Gold film modified carbon composite electrode | DP-CSV               | 4.0       | Fake template                     | Cr(VI)          | 2014                | [37]       |
| 29  | PET (4-pyridine-ethanethiol) | NaF 0.15 M (pH = 4.5)                | PET/nano-Au/Pt-RD electrode (Flower-like self-assembly of gold nanoparticles) AuNPs/GCE | DP-AdSV               | 0.001     | Seawater                          | Cr(VI)          | 2015                | [13]       |
| 30  | DTPA             | KH₂PO₄, Na₂HPO₄ (pH = 6–7)           | AuNPs/nano-TiC/GCE        | DP-CSV                 | 0.001     | Fake template                     | Cr(VI)          | 2012                | [38]       |
| 31  | HCl (pH = 2)     |                                     | AuNPs/SPCE                | DP-AdSV               | 2.08      | Seawater                          | Cr(VI)          | 2015                | [15]       |
| 32  | HClO₄ 0.06 M     |                                     | AuNPs/SPCE                | ASV                    | 0.002     | Tap water, seawater               | Cr(VI)          | 2015                | [39]       |
| 33  | QH2 (quercetin)  | Acetate buffer (pH = 6), KNO₃ 0.7 M | QH2/MWCNT-SPCE (quercetin/multiwalled carbon nanotubes screen-printed carbon electrode) | DP-AdSV               | 15.9      | Drinking water                    | Cr(VI)          | 2013                | [20]       |
| 34  | -                | Acetate buffer (pH = 5)              | µ NPs/GCE                 | DP-SV                  | 0.01      | Electroplating waste water        | Cr(III)         | 2015                | [44]       |
| 35  | DTPA 0.1 M       | Acetate buffer (pH 6), KNO₃ 0.25 M   | µ NPs/BiFE                | DP-AdSV               | 0.12. 10⁻³ | Fake template                     | Cr(VI)          | 2011                | [36]       |
| No. | Ligands | Background solution | Working electrode | Measurement techniques | LOD (pbb) | Analytical object | Determined form | Time of publication | References |
|-----|---------|---------------------|-------------------|------------------------|-----------|------------------|----------------|-------------------|------------|
| 36  | Polyvinyl butyral/SPEs + 4.7% DTPA | H₂SO₄ (pH 1) | SPEs (screen-printed electrode) | CV-AdSV | 52.0 | Fake template | Cr(VI) | 2014 | [42] |
| 37  | 2,5,8,11,14-Pentaaza-15,16,29-phenanthrolinophane (NeoTT) | 1.6-Dichloro-hexane (DCH), LiCl 10 mM, HCl 1 mM | Liquid/liquid interface | SqW-AdSV | 250.0 | Fake template | Cr(VI) | 2005 | [40] |
| 38  | | Silver: AgClO₄ 0.1 mM, briton robinson (pH 2) gold: HAuCl₄ 0.1 mM, H₂SO₄ 0.5 mM. | Carbon screen-printed electrode (CSPEs) | DPV | Silver: 44.2 gold: 20.8 | Fake template | Cr(VI) | 2008 | [43] |
| 39  | Septonex 10⁻⁶M (1-pentadecyltrimethylamonium bromide) | HCl 0.25 M, NaCl 0.1 M (pH < 2) | Carbon paste | DP-C CSV | 2.6 | Tea | CrO₄²⁻ | 2004 | [41] |
2.2. The Working Electrode and Adsorptive Stripping Voltammetric Procedure. In this method, the working electrode is bismuth film electrode created in *in situ* on glassy carbon rotating disk (*in situ* BiFE) and it is formed during the deposition process in the following way: The glassy carbon disk electrode was inserted into the electrochemical cell containing the reference electrode, platinum auxiliary electrode, and analysis solution (0.4·10⁻³ M DTPA, 28.8·10⁻³ M Bi(III), 5.0·10⁻⁶ M KBr, 0.4 M NaNO₃, 0.4 M acetate buffer solution, and Cr(VI)). The glassy carbon electrode was rotated with constant speed and deposition at −800 mV was observed (deposition voltage, *E*<sub>dep</sub>) at a definite time (deposition time, *t*<sub>dep</sub>); in the process, Bi(III) is reduced to Bi⁰ which adheres to the surface of glassy carbon plate forming *in situ* BiFE; at the same time, Cr(VI) is reduced to Cr(III), and then new Cr(III) forms complexes with DTPA in the solution layer close to the electrode surface and Cr(III)-DTPA complex adsorbed onto the surface of *in situ* BiFE, so chromium is enriched on the surface of *in situ* BiFE [10].

At the end of this period, the electrode stops rotating for 30–60 seconds (equilibration time, *t*<sub>eq</sub>). Subsequently, the potential scan was carried out in a negative potential direction from −800 mV to −1450 mV, and at the same time, the stripping voltammogram was recorded using a certain stripping voltammetry technique, differential pulse adsorptive stripping voltammetry (DP-AdSV), or square wave adsorptive stripping voltammetry (SQW-AdSV). During this period, Cr(III) in the Cr(III)-DTPA complexes is reduced to Cr(II) forming Cr(II)-DTPA complexes and generating the stripping peak current of chromium (*I*<sub>p</sub>) [10]. If NO₃⁻ is not present in solution, *I*<sub>p</sub> will be very small, NO₃⁻ present in the solution will oxidize Cr(II)-DTPA to Cr(III)-DTPA and then Cr(III)-DTPA is electrochemically reduced to Cr(II)-DTPA, and the repeated cycle increases the height of *I*<sub>p</sub> [10]. In other words, the NO₃⁻ ion acts as a catalyst. After dissolving, the electrode was cleaned by electrolysis at +400 mV for 30 seconds to dissolve Bi⁰ and other metals that may be present into the solution. *I*<sub>p</sub> is proportional to the concentration of Cr(VI) in the solution.

In all experiments, for Cr(VI) with trace, the first measurement result must be discarded because it is unstable. The stripping voltammogram was recorded 3 times (*n* = 3), and the peak current (*I*<sub>p</sub>) and peak potential (*E*<sub>p</sub>) values are averaged from three repetitions.

The glassy carbon electrodes were cleaned by polishing the surface with fine Al₂O₃ powder (particle size 0.6 µm) and then washed with distilled water and then with 1 M NaOH to remove all Al₂O₃ particles on the glassy carbon surface, and then the electrodes were dipped into 1 M HCl solution and finally washed with distilled water and the electrodes were dried with soft filter paper.

3. Results and Discussion

3.1. Differential Pulse Adsorptive Stripping Voltammetry (DP-AdSV) Using *In Situ* BiFE. In order to select the appropriate conditions for the method, the experimental conditions were fixed as shown in Table S1. A univariate method is applied to examine the effect of factors. The magnitude of the stripping peak current (*I*<sub>p</sub>) and the relative standard deviation of the *I*<sub>p</sub> (RSD) are used for selecting the appropriate test conditions.

3.1.1. Effect of Acetate Buffer Concentration. Acetate buffer is chosen to stabilize the pH of the solution. Acetate buffer is one of the factors that strongly influence the complex of Cr(III) and DTPA [10]. The complex formation between Cr(III) and DTPA usually occurs at pH = 6 [10, 11]. At chromium concentration *C*<sub>Cr(VI)</sub> = 3.8·10⁻⁸ M, ligand concentration *C*<sub>DTPA</sub> = 0.4·10⁻³ M, and bismuth concentration *C*<sub>Bi(III)</sub> = 24.10⁻⁵ M, the survey results of the effect of acetate buffer concentration (*C*<sub>Ac</sub>) in the range of 0.1 M–0.6 M (pH = 6) showed that *C*<sub>Ac</sub> = 0.4 M was appropriate. With this condition, the peak current is 31.36 µA and the repeatability is relatively good (RSD = 1.6% with *n* = 3) (Figure 1(a)).

3.1.2. Effect of Bi(III) Concentration and DTPA Concentration. Previous studies with *ex situ* BiFE electrodes have suggested that the presence of KBr in the solution increases the bismuth’s sustainability on the glassy disk surface and at the same time improves the conductivity of the solution [48]. In the acetate buffer with *C*<sub>Ac</sub> = 0.4 M and the presence of KBr at a concentration of 5.0·10⁻⁶ M, *C*<sub>DTPA</sub> = 0.4·10⁻³ M, and *C*<sub>Cr(VI)</sub> = 3.8·10⁻⁸ M, a Bi(III) concentration of 28.8·10⁻³ M is appropriate. At those concentrations, the peak current is 37.6 µA and the repeatability is good (RSD = 1.7% with *n* = 3) (Figure 1(b)). The survey results of the effect of DTPA concentrations in the range of 0.1 to 1.0·10⁻³ M to Cr peak current show that DTPA concentration of 0.4·10⁻³ M was appropriate (Figure 1(f)).

3.1.3. Effect of NaNO₃ Concentration. In the presence of NO₃⁻, peak current of chromium (*I*<sub>p</sub>) was enhanced significantly. Many authors argue that NO₃⁻ ions act as oxidizing agents that convert Cr(II)-DTPA complexes to Cr(III)-DTPA complexes and thus increase the concentration of Cr(III) on the electrode surface, and this leads to an increase in *I*<sub>p</sub> [10, 11, 21]. At *C*<sub>Ac</sub> = 0.4 M, *C*<sub>KBr</sub> = 5.0·10⁻⁶ M, *C*<sub>DTPA</sub> = 0.4·10⁻³ M, *C*<sub>Cr(VI)</sub> = 3.8·10⁻⁸ M, and *C*<sub>Bi(III)</sub> = 28.8·10⁻⁵ M, *I*<sub>p</sub> increased when the NaNO₃ concentration increased from 0.1 M to 0.4 M (Figures 1(e) and 2(c)). However, when the NaNO₃ concentration is greater than 0.4 M, it increases the baseline and may contaminate the analysis solution. When the NaNO₃ concentration is equal to 0.4 M, the peak current is 17.6 µA and the repeatability is quite good (RSD = 3.7% with *n* = 2). NaNO₃ concentration value of 0.4 M was selected for further investigation.

3.1.4. Effect of Deposition Potential (*E*<sub>dep</sub>) and Deposition Time (*t*<sub>dep</sub>). When *C*<sub>Ac</sub> = 0.4 M, *C*<sub>KBr</sub> = 5.0·10⁻⁶ M, *C*<sub>Cr(VI)</sub> = 2 ppb, *C*<sub>DTPA</sub> = 0.4·10⁻³ M, and *C*<sub>Bi(III)</sub> = 28.8·10⁻⁵ M, the survey results of the effect of the deposition potential in the range from −700 mV to −1000 mV are shown in Figure 1(c) and the stripping voltammetry is shown in Figure 2(a).
From this result, it shows that when $E_{\text{dep}}$ is equal to $-800 \text{ mV}$, the peak current is 42.1 $\mu\text{A}$ and the repeatability is good ($\text{RSD} \leq 1.3\%$ with $n = 3$). $E_{\text{dep}}$ of $-800 \text{ mV}$ was selected for further studies.

With the above conditions and when $E_{\text{dep}}$ is equal to $-800 \text{ mV}$, $I_p$ is almost unchanged when the deposition time ($t_{\text{dep}}$) is greater than 80 s, which means that it tends to reach saturation (Figure 1(d)). $t_{\text{dep}}$ of 50 s is selected for the next experiment (the stripping voltammetry at $t_{\text{dep}} = 50 \text{ s}$ is shown in Figure 2(b)).

3.1.5. Effect of Rotating Rate of Electrode ($\omega$) and Equilibration Time ($t_{\text{eq}}$). By increasing the rotation speed of the
electrode to a specified value, it will increase the mass transfer and the efficiency of the enrichment will be better. The survey results of the rotating rate of the electrode in the range from 800 rpm to 2400 rpm showed that $\omega$ of 2000 rpm was appropriate. At the end of the enrichment phase, the electrode should not be rotated for a specified period of time to keep the solution quiet and the electrode surface is stabilized (this time is also called equilibration time, symbolized as $t_{\text{equal}}$). $I_p$, survey results according to $t_{\text{equal}}$ showed that $t_{\text{equal}}$ of 50 s was appropriate.

### 3.1.6. Effect of Cleaning Potential ($E_{\text{clean}}$) and Cleaning Time ($t_{\text{clean}}$)

The cleaning of the surface of the carbon glassy disc electrode at the end of each stripping voltammetry is essential, as it will create repeating electrode surfaces for subsequent measurements. In terms of experimental conditions as in Section 3.1.3, the survey results of the influence of $E_{\text{clean}}$ in the range of 200 mV to 500 mV and $t_{\text{clean}}$ in the range of 60 s to 120 s showed that $E_{\text{clean}}$ is equal to 300 mV and $t_{\text{clean}}$ is equal to 110 s which are appropriate.

#### 3.2. Square Wave Adsorptive Stripping Voltammetry (SqW-AdSV) Using In Situ BiFE

Some authors argue that, in addition to differential pulse stripping voltammetry techniques, square wave stripping voltammetry can be used to record the signal (at this time, the method is called square wave adsorptive stripping voltammetry (SqW-AdSV)) and also allow the determination of very sensitive chromium. Based on the experimental conditions initially fixed as shown in Figure 1, the effects of the factors were investigated...
in a similar way to the DP-AdSV method, and we obtained the appropriate conditions for SqW-AdSV (using in situ BiFE) to determine Cr(VI) as shown in Table S2.

3.3. Interferences. Interferences for the determination of Cr(VI) consist of metallic cations that have the stripping peak current near the stripping peak current of chromium and anions that can form complexes or make conjugates with the forms of chromium and Bi(III) which can be adsorbed onto the surface of the in situ BiFE, and surfactants can be adsorbed onto the working surface of the electrode.

The influence of interferences can be estimated by relative error values of stripping peak current (RE). Consider that RE for \( I_p \) was equal to RE for C (because \( I_p = kC \)). RE for \( I_p \) (or C) was accepted when it was equal to \( \frac{1}{2} \) Horwitz function RSD (RE \( I_p(Cr) \) ≤ \( \frac{1}{2} \) RSD\(_{Horwitz} = \frac{1}{2}(1-0.5kC) = 32\% \) with \( C = 0.2 \) ppb). RE was calculated as follows:

\[
RE I_p(Cr) = \left( \frac{I_p(Cr) - I_p(Cr)^0}{I_p(Cr)^0} \right) \times 100, \tag{3}
\]

where RE is the relative error values of stripping peak current, \( I_p(Cr) \) is the stripping peak current without adding interferences and \( I_p(Cr)^0 \) is the stripping peak current with adding interferences.

3.3.1. Interference Studies. When the chromium(III) concentration is about 100 times higher than the chromium(VI) concentration, the \( I_p \) does not change significantly (RE < 18%). In fact, rarely encountered CRCr(III) case is 300 times higher than CRCr(VI), so it can be assumed that Cr(III) does not affect the Cr(VI) determination. This investigation again confirms that Cr(III) does not affect the determination of Cr(VI) (Table S3 and Figure S3).

In the acetate buffer (pH = 5–6), Zn(II), Co(II), and Ni(II) can affect the determination of Cr(VI) because it usually is used in order to observe the influence of the surfactant on the adsorption stripping voltammetry method. The effects of Triton X-100 (polyethylene glycol) is a typical nonionic surfactant and usually is used in order to observe the influence of the surfactant on the adsorption stripping voltammetry method. Triton X-100 does not affect the determination of Cr(VI) with RE < 27%.

In the adsorption stripping voltammetry method, the surfactant can be adsorptive on the surface of the working electrode, and this can affect the adsorption process of the metallic complexes on the working electrode. Triton X-100 (polyethylene glycol) is a typical nonionic surfactant and usually is used in order to observe the influence of the surfactant on the adsorption stripping voltammetry method. The effects of Triton X-100 are investigated at concentrations between 0 and 93.10^(-3) M, and the results in Table S6 show that, when increasing the concentration of Triton X-100 to 25 times higher than the concentration of Cr(VI), it still did not affect the determination of Cr(VI) with RE < 8%.

In fact, the concentration of natural surfactants is rarely greater than 77.10^(-3) M, and therefore, it can be assumed that they do not affect the Cr(VI) determination. Thus, when determining Cr(VI) by the adsorption stripping voltammetry method, it is not necessary to remove the surfactant from the analytical solution.

In some cases, natural water and wastewater contain many organic substances including surfactants. It is necessary to treat the sample to exclude organic substances before analysis using UV irradiation and decomposition in acid mixture.

3.4. Evaluation of Reliability of DP-AdSV and SqW-AdSV Methods

3.4.1. Repeatability. Repeat recording of 7 stripping voltammetry lines (n = 7) on the same in situ BiFE according to the DP-AdSV or SqW-AdSV method in Figure S3 shows that \( I_p \) in both approaches has good repeatability with RSD < 4% (n = 9) and RSD < 3% (n = 7), respectively, for DP-AdSV and SqW-AdSV. The stripping peak of chromium (\( E_p \)) is negligible, only about 20 mV toward the positive side.

3.4.2. Linear Range and Detection Limits. The linear range and LOD of the two methods SqW-AdSV and DP-AdSV
were investigated with the appropriate experimental conditions as shown in Table S2 and the stripping voltammetry specifications as shown in Table S1, and the following results were obtained:

1. **Linear Range.** For the SqW-AdSV method, $I_p$ and $C_{Cr(VI)}$ have a good linear correlation in the range $C_{Cr(VI)} = 0.3 \div 1.8$ ppb with a correlation coefficient ($R$) of 0.9994 (linear regression equation is shown in Figure 4(a), and the stripping voltammetry is shown in Figure 4(b)).

2. **Sensitivity.** The SqW-AdSV method achieved a sensitivity (23 $\mu$A/ppb) of about 34 times higher than the DP-AdSV (0.682 $\mu$A/ppb) method.

3. **Detection Limits and Quantitative Limits.** For SqW-AdSV (when $E_{dep} = -800$ mV and $t_{dep} = 160$ s): LOD = 0.1 ppb; LOQ = 0.3 ppb. For DP-AdSV (when $E_{dep} = -800$ mV and $t_{dep} = 50$ s): LOD = 0.6 ppb; LOQ = 2 ppb.

Thus, the SqW-AdSV method achieves a narrower linear range than the DP-AdSV method, but it achieves higher sensitivity than the DP-AdSV method (due to its lower LOD and greater slope linearity). It can be said that with LOD as above, DP-AdSV and SqW-AdSV methods can be used with in situ BiFE to determine the trace amount of Cr(VI).

3.5. **Determination of Chromium in Natural Water by the SqW-AdSV Using In Situ BiFE.** In natural water samples, chromium usually exists in both Cr(VI) and Cr(III) forms. As investigated, the SqW-AdSV/in situ BiFE method identifies Cr(VI) and also determines the total Cr(VI) + Cr(III) if during the decomposition of the sample, an additional oxidizer is added to oxidize Cr(III) to Cr(VI). Thus, we can determine chromium in individual forms by determining Cr(VI) (∗) and total chromium.

### Table 2: Influence of Zn(II), Co(II), and Ni(II) concentrations on peak current.

| Cation     | Zn(II) | Co(II) | Ni(II) |
|------------|--------|--------|--------|
| Cation (nM)| $I_p$ (Cr)(μA) | RE $I_p$(Cr)(%) | $C_{Cr(VI)}$(nM) | $I_p$ (Cr)(μA) | RE $I_p$(Cr)(%) | $C_{Cr(VI)}$(nM) | $I_p$ (Cr)(μA) | RE $I_p$(Cr)(%) |
|-----------|---------|--------|--------|
| 1         | 0       | 96.4   | 0      | 0       | 76.5   | 0      | 0       | 49.7   |
| 2         | 770     | 96.3   | 0.1    | 84      | 82.4   | 7.6    | 84      | 53.2   |
| 3         | 1540    | 94.6   | 1.9    | 168     | 82.5   | 7.9    | 168     | 58.3   |
| 4         | 2310    | 87.9   | 8.7    | 252     | 81.7   | 6.8    | 252     | 61.5   |
| 5         | 3080    | 80.9   | 16.0   | 336     | 77.8   | 1.7    | 336     | 62.4   |

Conditions: $C_{Cr(VI)} = 3.8 \times 10^{-7}$ M = 0.2 ppb; $C_{Bi(III)} = 2.8 \times 10^{-5}$ M; $t_{ad} = 120$ s; $E_{clean} = 400$ mV; $t_{clean} = 100$ s; $U_{step} = 6$ mV; $v = 210$ mV/s; $\Delta E = 30$ mV; $f = 35$ Hz; $\omega = 2000$ rpm; $C_{DTPA} = 0.4$ mM; $C_{Al} = 0.4$ M; $C_{NaNO3} = 0.4$ M; $E_{ad} = -800$ mV.
Cr(VI) (+ III) (**). It follows that the Cr(III) content is the difference of (***) and (*).

Based on the above results, it is possible to apply the SqW-AdSV/\textit{in situ} BiFE to determine the trace of Cr(VI) with LOD \(\approx 0.1\) ppb. With that LOD, the SqW-AdSV/\textit{in situ} BiFE can directly determine the amount of Cr(VI) in natural water, without the stage of getting rich, and this is a great advantage of the SqW-AdSV/BiFE method.

\[ I_p = 44.50 + 23.19 \times [\text{Cr(VI)}] \]
\[ R = 0.9994 \]

\[ I_p = 0.89 + 0.68 \times [\text{Cr(VI)}] \]
\[ R = 0.9989 \]
Table 4: Accuracy of the SqW-AdSV/in situ BiFE for the determination of chromium in surface water.

| Information | \([\text{Cr(VI)}](\text{ppb})\) | \(C_{Cr}\) (ppb) |
|-------------|----------------|----------------|
| Experiment 1 | 0.38           | 1.90           |
| Experiment 2 | 0.40           | 2.00           |
| Experiment 3 | 0.40           | 2.00           |
| Average ± S (ppb) |               | 1.97 ± 0.08    |
| Cr content in the CRM sample (ppb) | 2.00 ± 0.02 \((C_{Cr} = 1.98 ± 0.02 \text{ppb})\) |
| RSD (%) | 4               |

\(^{[3]}\text{[Cr(VI)]}\) is the concentration of Cr(VI) in the electrolyte minus the blank. White sample has \([\text{Cr(VI)}] = 0.034 \text{ppb}\); \(C_{Cr}\) is the Cr content in the sample (calculated by the formula: \(C_{Cr} = [\text{Cr(VI)}] / \left(V_2 / V_1\right)\). \(V_1\): volume of solution taken into the electrolyser \((V_1 = 2 \text{mL})\), \(V_2\): volume of solution in the electrolyser \((V_2 = 10 \text{mL})\), \(S\) is the standard deviation. Experimental conditions are as shown in Table 3.

Table 5: Determination of the accuracy of the SqW-AdSV/in situ BiFE on the NASS 6.

| [NAAS 6] | The content of chromium in the sample (ppb) \(\times 1\) | Chromium standard added (ppb) \(\times 0\) | The content of chromium in standard added samples (ppb) \(\times 2\) | Recovery (%) |
|----------|-----------------------------------------------------|----------------------------------------|-----------------------------------------------------|-------------|
| 2 ppb    | 0.116                                               | 1.884                                  | 1.915                                               | 96          |
|          |                                                     |                                        | 2.043                                               | 102         |
|          |                                                     |                                        | 1.941                                               | 97          |
| Average ± S |                                               |                                          | 1.966 ± 0.054                                      |             |
| 6 ppb    | 0.116                                               | 5.884                                  | 5.958                                               | 99          |
|          |                                                     |                                        | 6.258                                               | 104         |
|          |                                                     |                                        | 5.655                                               | 94          |
| Average ± S |                                               |                                          | 5.957 ± 0.213                                      |             |
| 10 ppb   | 0.116                                               | 9.884                                  | 10.687                                              | 107         |
|          |                                                     |                                        | 10.125                                              | 101         |
|          |                                                     |                                        | 10.887                                              | 109         |
| Average ± S |                                               |                                          | 10.566 ± 0.279                                      |             |

\(^{[3]}\)Recovery = \((x_2−x_1)\cdot 100/x_0; S\) is the standard deviation; experimental conditions are as shown in Table 3.

3.5.1. Quality Control of Analytical Methods through Standard Sample Analysis. In order to confirm the practical applicability of the SqW-AdSV method to analyze chromium traces using BiFE electrodes, it is necessary to control the analytical method quality by evaluating the accuracy and repeatability when analyzing standard samples.

(1) For Surface Water Samples. Surface water Certified Material Reference (SPS-SW1 Batch 122) was selected to evaluate the accuracy of the method. The actual value of the chromium content of the sample is 2.00 ± 0.02 ppb (95% confidence boundary \(e = ± 0.02 \text{ppb}\)). Analysis of standard SPS-SW1 surface water (CRM) samples by the SqW-AdSV using in situ BiFE with the appropriate experimental conditions is shown in Table 3. The analysis was repeated 3 times. The volume of the solution to be charged to the electrolyser is 2 mL, and the volume of solution in the electrolyser is 10 mL.

The results in Table 4 show that the SqW-AdSV/in situ BiFE has good repeatability (the standard deviation is 4%) for the repetition of 3, and it is less than half the standard deviation based on the Horwitz function \(\text{RSD}_{H} = 2^{(1−0.5\lg e)}\), when the chromium concentration is 2 ppb, the standard deviation of the Horwitz equation is 41% \([49]\) and the method has good accuracy because the chromium content is within the 95% confidence interval of the CRM sample.

(2) For Seawater Samples. Analysis of the standard seawater CRM coded NASS 6 by the SqW-AdSV/in situ BiFE with the appropriate experimental conditions as shown in Table 3.

Because the concentration of chromium in NASS 6 seawater was too small to be directly analyzed, only NASS 6 standard sample was used as the matrix for analysis and validity. The actual value of the chromium content in the NASS 6 sample is 0.116 ± 0.008 ppb (the 95% confidence bound \(e = ± 0.008 \text{ppb}\)). NASS 6 standard sample was added with standard Cr(VI) solution to attain 3 levels of 2 ppb, 6 ppb, and 10 ppb and then analyzed with the standard added samples to determine recovery.

The results showed that the SqW-AdSV/in situ BiFE for chromium analysis in seawater samples has a good accuracy (recoverability from 94 to 109%). According to the AOAC (American Association of Analytical Chemists) when analyzing the levels of 1.0 to 10 ppb, achieving a recovery rate of 80 to 110% is acceptable \([50]\). Therefore, it is possible to use this method to analyze chromium in seawater samples (Table 5).

The results of the linear range, sensitivity, limit of detection, and accuracy showed that it is possible to use
SqW-AdSV/in situ BiFE to determine chromium in surface water and seawater.

3.5.2. Real Sample Analysis. For the purpose of testing the possibility of applying the SqW-AdSV/in situ BiFE method for the analysis of chromium in water environment, well water, tap water, lagoon water, and seawater in some different areas in Thua Thien Hue province were taken for analysis. Watersamples were taken in clean PET bottles and acidified with concentrated HCl (500 μl HCl/500 ml of sample). Samples were filtered through 0.45 μm porous fiberglass filter paper and analyzed immediately after filtration.

Collected and stored samples were analyzed directly (after filtration through a 0.45 μm porous fiberglass paper) to determine the Cr(VI) content by the SqW-AdSV/in situ BiFE; the total chromium content of the sample was determined after the decomposition of the sample by the method of (a) ((a): add 50 μl of concentrated HCl, 25 μl of H2O2 35% to 50ml of sample in the Teflon cup, boil for 90 minutes, let it cool, and adjust up to 25ml) [51].

Samples were analyzed by SqW-AdSV/in situ BiFE according to the process shown in Figure S2. The results of actual sample analysis are presented in Table 6.

4. Conclusion

Using in situ BiFE electrodes with DTPA complexing ligands in acetate buffer solution pH 6 with the presence of KBr and NO3- ion, DP-AdSV and SqW-AdSV methods can determine chromium(VI) concentrations of 0.3 ppb and 2.0 ppb, respectively. The proposed method has been successfully applied for chromium analysis in some natural water samples such as lagoon water, well water, tap water, and seawater in some areas of Thua Thien Hue province, Vietnam. This C_{Cr(VI+III)} analysis procedure in water sample by SqW-AdSV/in situ BiFE method was satisfactorily applied for the determination of chromium in real water such as tap water, river water, and well water samples in all countries of the world. The determination of chromium in the above real water sample could be carried out within 60 min.

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.

Supplementary Materials

Table S1: for the DP-AdSV and SqW-AdSV using in situ BiFE. Table S2: suitable experimental conditions for DP-AdSV and SqW-AdSV methods using in situ BiFE. Table S3: influence of chromium(III). Figure S1: SqW-AdSV/BiFE in situ stripping voltammograms of chromium(VI) when examining the effects of chromium(III). Table S4: influence of Fe(III) and Ca(II). Table S5: influence of Cl− and SO42−. Table S6: influence of Triton X-100. Figure S2: diagram of C_{Cr(VI+III)} analysis procedure in water sample by SqW-AdSV/in situ BiFE method. . (Supplementary Materials)

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