Journal of
*Marine Science
and Engineering*

MDPI

Article

Field Determination and Spatial Distribution of Se (IV) in Coastal Seawater of China

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Abstract: A portable electrochemical system based on rGO/AuNPs/Nafion was constructed for selenium (IV) field determination in coastal seawater of the North Yellow Sea, East China Sea and South China Sea. This system demonstrated a low determination limit (0.03 µg/L), a wide linear range of concentration (0.1–30 µg/L), exceptional reproducibility and repeatability, and excellent selectivity. Each individual, entire test could be accomplished within 8 min. In Yantai Sishili Bay, the Se (IV) concentrations ranged from 0.16–3.59 µg/L (average 1.43 µg/L). In Shengshan Island, the Se (IV) concentrations ranged from 0.20–5.18 µg/L (average 2.06 µg/L). In Zhelin Bay, the Se (IV) concentrations ranged from 0.87–4.87 µg/L (average 3.13 µg/L). The average concentrations of Se (IV) in surface seawater showcased an increasing trend from the north to the south of China, suggesting Zhelin Bay > Shengshan Island > Sishili Bay. The system develops a new, competitive method for water quality assessment, and contributes to the accurate study of the biogeochemical cycles of selenium.

Keywords: selenium; electrochemical system; field determination; seawater

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Citation: Liu, T.; Pan, D.; Wei, H.; Liang, Y.; Li, Y.; Rahman, M.A. Field Determination and Spatial Distribution of Se (IV) in Coastal Seawater of China. *J. Mar. Sci. Eng.* **2024**, *12*, 398. https://doi.org/10.3390/jmse12030398

Academic Editor: Gianluca Quarta

Received: 30 January 2024
Revised: 23 February 2024
Accepted: 23 February 2024
Published: 26 February 2024

1. Introduction

Selenium is a naturally occurring metalloid element and a micronutrient essential for the growth of many organisms, including humans. Selenium is also known as a "double-edged element", because it has a very narrow threshold between nutritional deficiencies (40 µg/d) and toxic levels (400 µg/d) [1]. Total dissolved selenium (TDSe) in natural water exhibits complex behavior as it exists in multiple oxidation states (-II, IV, and VI) and participates in a variety of complex biogeochemical cycling processes [2–5]. Selenium has antioxidant, anticancer and antagonistic effects against heavy metals. Selenium deficiency can lead to cirrhosis of the liver, cancer, etc., but excess selenium in the environment can in turn be toxic, especially to aquatic oviparous organisms, with teratogenic effects, thus affecting ecosystem populations as a whole [6]. In addition, selenium can bioaccumulate and is eventually transferred to the human body through the food chain. Studies have proven that excessive selenium can lead to gastrointestinal disorders, hair loss, and neurological dysfunction [7]. In studies of the physicochemical behavior, toxicological risks, and bioavailability of elements, it has been found that in many cases it would be more meaningful to determine the toxic form of a substance [8]. In the marine environment, selenium is usually found in the form of Se (IV) and Se (VI) oxygen anions, which are up to 40 times more toxic than organic substances [9]. Of these, laboratory studies have shown

Se (IV) to be 20 times more toxic than Se (VI), due to its higher bioavailability and better mobility [10]. Se (VI) is not electroactive compared to Se (IV) [11]. It has been demonstrated that the concentrations of electrochemically active elements, as determined by dissolution voltammetry, are consistent with the concentrations of bioavailable elements. Therefore, from the perspectives of marine management, ecological safety, and human health, it is necessary and urgent to establish a reliable, rapid, and sensitive analytical method to accurately detect Se (IV) in the marine environment.

Currently, selenium is analyzed by a variety of methods, including Atomic Fluorescence Spectrophotometry (AFS) [12], Hydride Generation Atomic Absorption Spectrometry (HG-AAS) [13,14], Inductively Coupled Plasma Mass Spectrometry (ICP-MS) [15–17], Capillary Electrophoresis (CE) [18–20], and Inductively Coupled Plasma Emission Spectrometry (ICP-OES) [21], which are all techniques used by various regulatory agencies. These traditional methods are limited to laboratory measurements. They suffer from the disadvantages of expensive instrumentation and complex pre-treatment, and are not specifically designed for field applications [22,23]. Studies have shown that phytoplankton and microorganisms in seawater environments preferentially take up Se (IV) [24,25]. In addition, temperature affects the ratio between Se (IV) and Se (VI) [26]. Laboratory measurements of Se (IV) can be affected by microorganisms as well as temperature, in addition to possible contamination of samples during sampling transportation, which can affect the concentration of Se (IV) in actual seawater samples. Therefore, it is necessary to develop a method for the direct and rapid determination of Se (IV) in seawater in the field.

Electrochemical methods are a viable method for the field determination of Se (IV). It has the advantages of low cost, simplicity of use and operation, and high sensitivity, which can compensate for some of the shortcomings of traditional methods to a certain extent [27,28]. Notably, electrochemical methods can be used to design portable analyzers whose performance depends mainly on the modified materials on the electrode surfaces. Nanomodified materials excel in increasing sensitivity and decreasing the determination limit of electrochemical systems [29]. Among various types of nanomaterials [30], gold nanoparticles (AuNPs) have been used as the material of choice for the design of electrochemical systems due to their efficient mass transfer capability, strong catalytic ability, and good signal-to-noise ratio [31]. Reduced graphene oxide (rGO) is a new type of carbon material produced by reducing graphene oxide. The rGO can increase the specific surface area of the electrodes, allowing more AuNPs to be deposited on the electrode surfaces, which can, to a certain extent, increase the determination range of electrochemical systems. However, the rGO contains a large number of hydrophilic groups, which are difficult to separate from water in seawater and tend to agglomerate [32,33]. Therefore, the addition of perfluorosulfonic acid (Nafion) [34] can accelerate ion exchange to a certain extent and form a stable film on the electrode surface to compensate for the shortcomings of rGO. Although similar methods have been previously reported for the determination of Se (IV), the determination of Se (IV) is still focused on the laboratory environment, and there are no methods for reliable and rapid field determination of Se (IV) [35].

The objective of this study was to construct a portable electrochemical system for field determination of Se (IV) with a transition from lab-based optimization to field implementation of the developed methodology, which could be used for field determination to achieve rapid determination of Se (IV). In this work, a portable electrochemical system was constructed with a glassy carbon electrode modified with rGO/AuNPs/Nafion composite as the working electrode. The determination performance was investigated by differential pulse dissolution voltammetry (DPV) under optimal experimental conditions and the experimental results were compared with AFS. Meanwhile, in order to validate the practicality of the constructed portable electrochemical system for field determination of Se (IV), we chose three representative areas of offshore China. These include Yantai Sishili Bay in the North Yellow Sea, Shengshan Island in the East China Sea, and Zhelin Bay in the South China Sea. This demonstrates that the constructed portable electrochemical system could achieve reliable and stable field determination of Se (IV).

2. Experimental Section

2.1. Reagents

Unless otherwise stated, all the chemical reagents used in this study were analytical grade and provided by Sinopharm Chemical Reagent Co., Ltd., (Shanghai, China). Graphene oxide (GO, 1–5 μm diameter, 0.8–1.2 nm thickness, purity > 99%) provided by Nanjing JC Nano Technology Co., Ltd. $HAuCl_4 \cdot 4H_2O$ provided by Sinopharm Chemical Co., Ltd., Nafion (5 wt%, in a mixture of lower aliphatic alcohols and water, contains 45% water) provided by Sigma Co., Ltd., (Shanghai, China). $HClO_4$ and Se (IV)standard solutions provided by Acros Organics. Deionized water (18.2 MΩ cm specific resistance) obtained with a Pall Cascada laboratory water system was used throughout. Standard artificial seawater (salinity of 34.999) was purchased from Beijing Putian Tongchuang Biological Technology, Co. (Beijing, China). The experimental vessels were washed and soaked in 1M HNO_3 acid washing solution for at least 24 h, washed with ultrapure water, and then dried and set aside.

2.2. Apparatus

The morphologies of the modified electrodes were characterized by scanning electron microscopy (SEM, Hitachi, Ltd., Tokyo, Japan). Atomic fluorescence spectrophotometry (AFS-8530, Hai Guang Instrument Co., Beijing, China) was used for the comparative determination of selenium. All electrochemical experiments were performed in a conventional three-electrode electrolytic cell controlled by an electrochemical workstation (CHI 1230C CH Instruments, Inc., Shanghai, China). A glassy carbon electrode was used as the working electrode, Ag/AgCl as the reference electrode and Pt electrode as the auxiliary electrode.

2.3. Construction of Portable Electrochemical System

The construction of a portable electrochemical system for field determination of Se (IV) is shown in Figure 1, which consists of three main parts: (1) a laptop computer; (2) a portable electrochemical workstation; (3) a three-electrode electrolytic cell system consisting of a glassy carbon electrode modified with rGO/AuNPs/Nafion composites as the working electrode, Ag/AgCl as the reference electrode, and a platinum electrode as the auxiliary electrode.

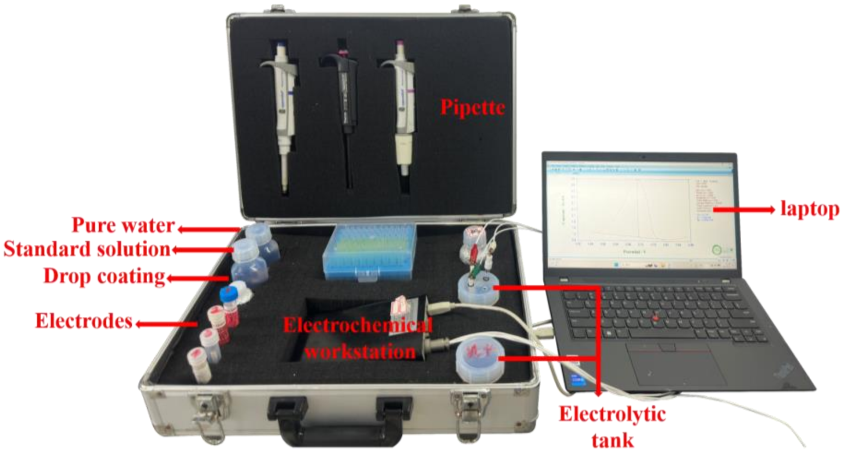

Figure 1. Images of the constructed portable electrochemical system.

2.4. Electrochemical Analysis Procedure

Two electrolytic cells were prepared for both experiments, one for the reduction of the surface modification material of the working electrode, the other for the determination of Se (IV). In addition, GO, $HAuCl_4$ and Nafion were mixed in the ratio of 1:3:1 by volume and then ultrasonically dispersed for 8 h to obtain a homogeneous GO/$HAuCl_4$/Nafion suspension and then shaded and set aside. First, thirty milliliters of pure water was taken in a three-electrode electrolytic cell using a micropipette gun, and the successfully prepared rGO/AuNPs/Nafion composite solution-modified working electrodes were reduced for 10 s using the Amperometric i-t Curve (i-t) at a voltage of −0.5 V. Next, thirty milliliters of the solution to be tested was taken in a three-electrode electrolytic cell using a micropipette gun, and $HClO_4$ was added to make the concentration of 1 M. The determination steps were as follows: (1) use of the i-t enrichment was carried out for 300 s under the potential condition of −0.5 V, so that Se (IV) was deposited on the surface of the working electrode modified with the rGO/AuNPs/Nafion composite material; (2) using the DPV method (amplitude 0.05 V, pulse period 0.5 s, equilibrium time 0.2 s) to record the dissolution voltammograms under the potential condition of 0.55–0.95 V. The DPV was performed at a potential of 0.5 V–0.95 V. The experiments were performed using the DPV for the determination of Se (IV) unless otherwise stated, and the experimental procedure is simple, requiring 8 min of detecting.

2.5. Determination of Se (IV) in Real Seawater Samples

Seawater samples were collected from north to south along the coastline of China from Yantai Sishili Bay in the North Yellow Sea, Zhoushan Shengshan Island in the East China Sea, and Chaozhou Zhelin Bay in the South China Sea. The samples obtained all belonged to the open coastal seawater near Chinese coastal ports or aquaculture areas, surrounded by urban buildings and closely affected by human activities. Yantai Sishili Bay is a relatively enclosed bay located in the North Yellow Sea, bordering Yantai, which is an important port city and fishery base in China. Shengshan Island is located in Zhoushan City, Zhejiang Province, at the easternmost point of Shengsi Islands, beyond the mouth of the Yangtze River, and its archipelago is adjacent to Hangzhou Bay, which neighbours Shanghai City by the cross-sea bridge. Shengsi County, one of the top ten fishery counties in the country, is located in the center of the famous Zhoushan fishery, and it is also an important combination port of Ningbo-Zhoushan Port, and is the core port area of the Shanghai International Shipping Center. Although the port and fishery industries drive the development of the local economy, they also lead to the Yantai Sishili Bay and Shengshan Island area facing a huge pressure from shipping, fishery, aquaculture, and other human activities, which have certain impacts on the ecological safety of the sea area. In addition, Zhelin Bay is a bay along the South China Sea in northeastern Guangdong, which is the largest seawater aquaculture area and the most densely managed coastal aquaculture pond area in eastern Guangdong. Seawater aquaculture occupies half of the seawater in Zhelin Bay, which has greatly contributed to the development of the local economy but also accelerated the rate of seawater pollution, such as eutrophication, in the waters. Therefore, based on the above reasons, it is very necessary and urgent to carry out the determination of various indicators in its sea area. All seawater samples were collected and filtered through a 0.45 μm membrane filter and then stored, first in acid-washed PTFE bottles to which $HClO_4$ was added to adjust the seawater sample pH 2.0. The Se (IV) of the actual samples was detected using rGO/AuNPs/Nafion/GCE as working electrodes according to the i-t and DPV, as described previously.

2.6. Software Used

Electrochemical and concentration correlation plots were produced by Sigma Plot 12.5 and Origin 2021 software. The site locations throughout the article were applied to Ocean Data View version 5.5.1 (https://odv.awi.de/ (accessed on 9 June 2023)).

3. Results and Discussion

3.1. Characterization of Working Electrodes of Portable Electrochemical Systems

The morphological structure of the rGO/AuNPs/Nafion modified electrode was characterized using SEM, which is shown in Figure 2A,B. The surface of rGO was corrugated and partially curled with uniform AuNPs, and the Nafion was also uniformly covered on its surface. The composition of the rGO/AuNPs/Nafion was analyzed by EDS, and is shown in Figure 2C. The EDS results indicated that C, O, F and Au were the major constituent elements of the prepared electrode. Among them, C and O were mainly from rGO, F was all from Nafion, and Au was all from AuNPs. The results demonstrated that the rGO/AuNPs/Nafion composites were successfully modified on the electrode.

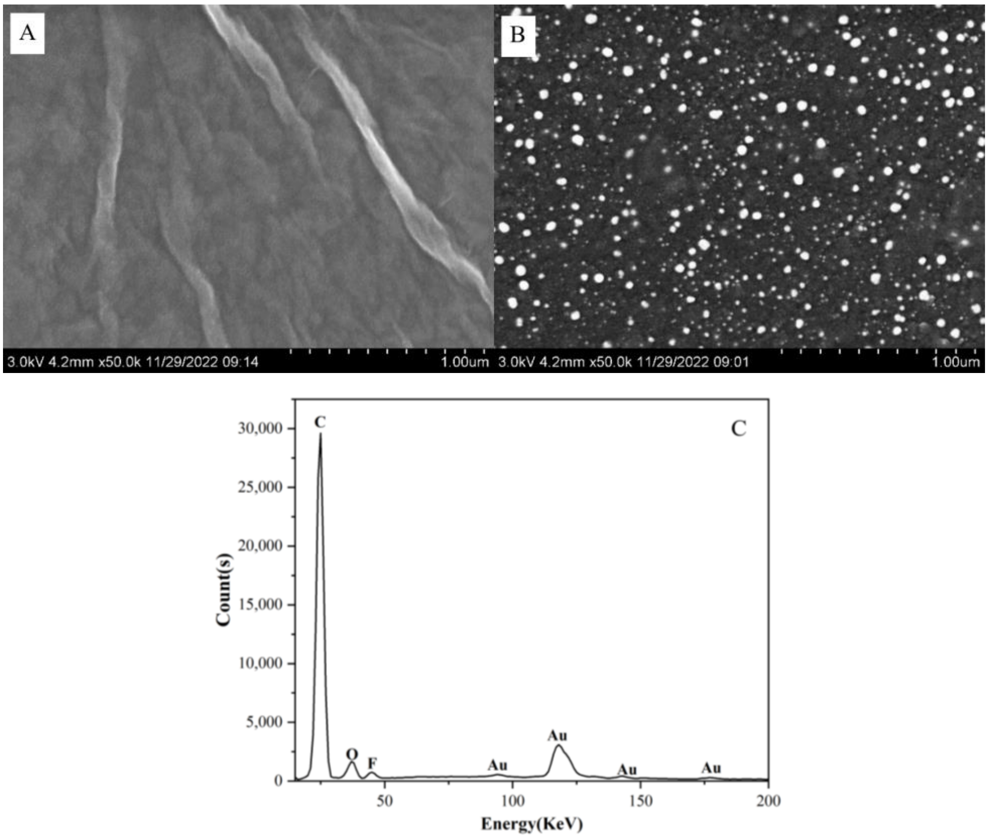

Figure 2. (**A**,**B**) SEM images of rGO and rGO/AuNPs/Nafion; (**C**) EDS spectrum of rGO/AuNPs/Nafion.

3.2. Electrochemical Behaviors of Working Electrodes for Portable Electrochemical System

The electrochemical response signals of the bare electrode, Nafion/GCE, rGO/GCE, AuNPs/GCE and rGO/AuNPs/Nafion/GCE were analyzed by cyclic voltammetry (CV) in 5 mM $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ electrolyte solutions containing 0.1 M KCl, and the results are shown in Figure 3A. The size of the redox peak is proportional to the specific surface area of the electrode, under the same experimental conditions. The rGO has a larger specific surface area, which can increase the redox current peak of the modified electrode. In addition, the excellent adhesion of Nafion to the electrode surface led to the formation of a stable film, which improved the response of CV and also prevented $[Fe(CN)_6]^{3-/4-}$ diffusion on the electrode surface. Therefore, the rGO/AuNPs/Nafion composite-modified electrodes have good capacitive performance and catalytically active surfaces. The results of the selection of Nafion/GCE, rGO/GCE, AuNPs/GCE, and rGO/AuNPs/Nafion/GCE by DPV in standard seawater containing 10 μg/L Se (IV) standard solution are shown in Figure 3B. Se (IV) showed no significant response signal to bare electrodes, under the same experimental conditions. However, Se (IV) showed the maximum peak current for rGO/AuNPs/Nafion/GCE due to the good synergy between AuNPs and rGO.

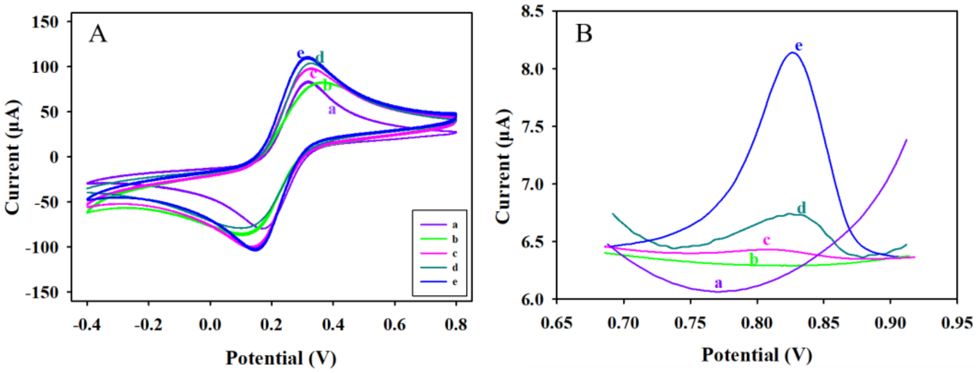

Figure 3. (**A**) The CV of bare GCE (a), Nafion/GCE (b), rGO/GCE (c), AuNPs/GCE (d), rGO/AuNPs/Nafion/GCE (e) in 5 mM [Fe $(CN)_6]^{3-/4-}$ solution containing 0.1 M KCl; (**B**) the DPV of bare GCE (a), Nafion/GCE (b), rGO/GCE (c), AuNPs/GCE (d), rGO/AuNPs/Nafion/GCE (e) in standard seawater spiked with 10 μg/L Se (IV).

3.3. Performance Analysis of Portable Electrochemical System for Se (IV) Determination

3.3.1. Optimization of Experimental Parameters

To obtain better analytical performance in the determination of Se (IV), the main experimental conditions were optimized in a standard seawater solution spiked with 10 μg/L Se (IV), and the results are shown in Figure 4. The relationship between the response of rGO/AuNPs/Nafion/GCE to Se (IV) and the drop coating amount of the modifier is shown in Figure 4A, which shows that the response signal gradually increases with the increase of the drop coating amount from 1–5 μL, but gradually decreases after more than 5 μL. The main reason may be that the rGO/AuNPs/Nafion composite is easy to fall off with too much attachment; in addition, the increase in the thickness of the Nafion film also leads to the weakening of the response signal, so a drop coating volume of 5 μL was chosen for the determination of Se (IV).

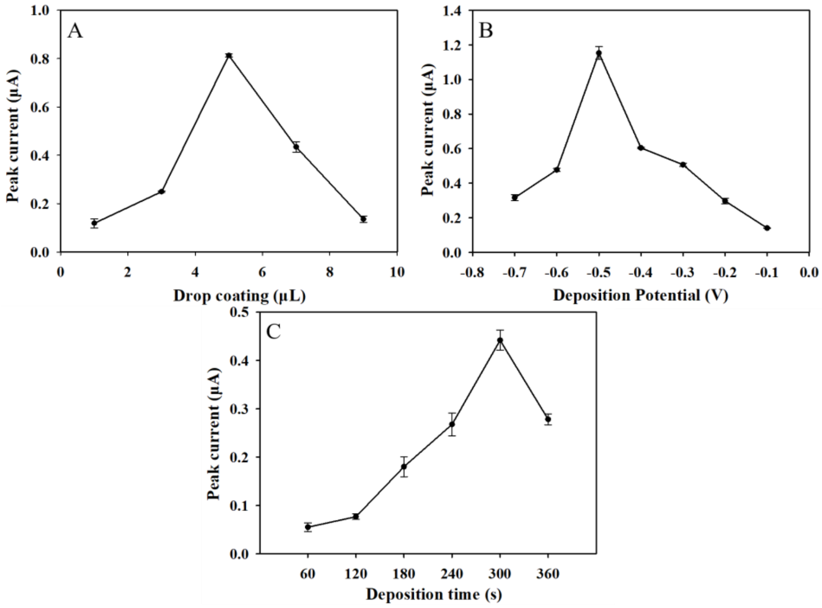

Figure 4. (**A**) Effect of Se (IV) deposition time, (**B**) the Se (IV) deposition potential, (**C**) the rGO/AuNPs/Nafion drop coating amount on response current in a standard solution of 10 μg/L Se (IV) (n = 3).

To obtain a better stripping response, the deposition potential of Se (IV) on the modified electrode was investigated in the range of −0.8–0 V. The results are shown in Figure 4B, where it can be seen that the deposition potential at −0.5 V exhibits a better current response. The main reason may be that Se (IV) with a positive charge at −0.8–0.5 V exhibits a gradual enhancement of adsorption tendency on the surface of the modified electrode because rGO/AuNPs/Nafion has a negative charge; however, as the potential continues to increase at −0.5–0 V, the response current gradually decreases, which may be since there is not enough Se (IV) adsorbed on the surface of the modified surface of the electrode. Therefore, a potential of −0.5 V was chosen for Se (IV) determination.

To obtain the optimal deposition time, the effect of deposition time on the response current was explored in the range of 60–300 s, and the results are shown in Figure 4C, where it can be seen that the response current of the Se (IV) peak is gradually enhanced with the increase of deposition time in the range of 60–300 s, and then gradually weakened. The main reason may be that the deposited Se (IV) increases with time and may be partially detached under acidic conditions. Therefore, 300 s was selected as a suitable time.

3.3.2. Calibration Features

In seawater, Se exists mainly in tetravalent and hexavalent forms, but Se (IV) is the only electroactive form. Under optimal experimental conditions, selenium is usually considered to be susceptible to the following reactions when it is electrically reduced in acidic media through higher negative potentials:

$$H_2SeO_3 + 4H^+ + 4e^- \rightarrow Se + 3H_2O \tag{1}$$

$$H_2SeO_3 + 6H^+ + 6e^- \rightarrow H_2Se + 3H_2O \tag{2}$$

$$H_2SeO_3 + 2H_2Se \rightarrow 3Se + 3H_2O \tag{3}$$

Selenite will occur preferentially in acidic media by applying the negative potential Equation (2), however, H_2Se cannot be stabilized in solution and will react rapidly with H_2SeO_3 to form Se (0). Although Se (IV) may undergo different reduction mechanisms at the electrode surface, the net process at the electrode surface is the reduction of Se (IV) to Se (0); then a stripping reaction occurs at the electrode surface that transforms Se (0) to Se (IV). Under the optimal experimental conditions, the calibration curve of Se (IV) was plotted using the DPV method, as shown in Figure 5, which shows that the peak current shows a good linear relationship with the Se (IV) concentration within 0.1–30 μg/L. The linear regression equation was $Ip = 0.1832c + 0.0028$ ($R^2 = 0.998$), and the determination of the rGO/AuNPs/Nafion modified electrode with the determination limit of Se (IV) was 0.03 μg/L. In addition, a comparison of the analytical performance between the method used in this study and some other analytical methods is presented in Table 1. The rGO/AuNPs/Nafion modified electrode is a good choice for the determination of Se (IV) because of its higher sensitivity, lower limit of determination, and wider linear range than other methods.

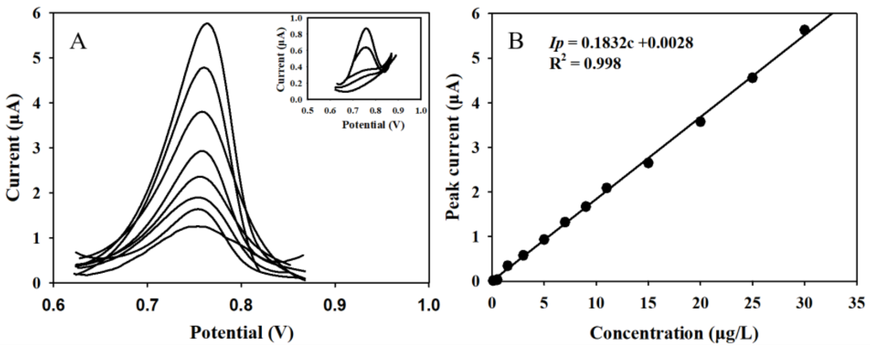

Figure 5. (**A**) The DPV of the rGO/AuNPs/Nafion/CGE in standard seawater sample containing 0, 0.1, 0.5, 1.5 and 3 μg/L (inset) and 5, 7, 9, 11, 15, 20, 25 and 30 μg/L Se (IV) (from bottom to top); (**B**) the calibration curve for Se (IV) determination.

Table 1. Comparison of the developed electrochemical sensing system and other analytical methods.

Methods [a]	Electrode [b]	Linear Range (µg/L)	LOD (µg/L)	Samples	Reference
CE-ICP-MS	No	10–400	2.31	Surface water	[36]
FI-HG-AFS	No	0.02–2	0.005	Surface water	[37]
CP-FI-HG-ICP-OES	No	0.03–200	0.03	River water	[38]
SPME-HG-AAS	No	0.0012–200	0.004	River water	[39]
DPCSV	HMDE	0.6–16	0.06	River water	[40]
DPCSV	HCADE	0.02–2.8	0.02	Tap water	[41]
adsDPCSV	BiHg/GCE	2–50	0.07	Sea water	[42]
SWASV	AuNPs/GCE	10–50	0.52	Sea water	[43]
DPASV	rGO/AuNPs/Nafion/GCE	0.1–30	0.03	Sea water	This work

[a]: adsDPCSV: Adsorptive Differential Pulse Cathodic Stripping Voltammetry; AAS: Atomic Absorption Spectrometry; AES: Atomic Emission Spectrometry; AFS: Atomic Fluorescence Spectrometry; CE: Capillary Electrophoresis; DPASV: Differential Pulse Anodic Stripping Voltammetry; DPCSV: Differential Pulse Cathodic Stripping Voltammetry; HG: Hydride Generation; HPLC: High-Performance Liquid Chromatography; ICP: Inductively Coupled Plasma; MS: Mass Spectrometry; SWASV: Square Wave Anodic stripping Voltammetry. [b]: HCADE: Hanging Copper Amalgam Drop Electrode; HMDE: Hanging Mercury Drop Electrode.

3.4. Reproducibility, Repeatability and Selectivity

Three independent rGO/AuNPs/Nafion/GCE were prepared by the same method and detected in the same electrolyte solution, and the relative standard deviation (RSD) between the three electrodes was 4.6%. In addition, each electrode was subjected to seven consecutive tests under the same conditions, and the RSDs of the three electrodes were 8%, 9.1%, and 7.2%. The experimental results showed that the rGO/AuNPs/Nafion/GCE had good reproducibility and repeatability

Other ions in the complex matrix may interfere with the rGO/AuNPs/Nafion electrode. To investigate the effect of possible interfering substances on the determination of elemental selenium, various exotic species were added to a standard seawater sample solution containing 5 µg/L Se (IV). The determination of Se (IV) was not significantly interfered with by 100 times of Cd^{2+}, Ni^{2+}, Pb^{2+}, Cu^{2+}, Sn^{2+} and Zn^{2+} and 50 times of Fe^{3+}(<5% change in the corresponding currents), indicating that the modified electrodes are valuable for the determination of Se (IV) in real seawater environment.

3.5. Practical Application

To validate the accuracy of the developed portable electrochemical sensing system, the developed electrochemical sensing system and AFS were used to detect the TDSe in real samples under the optimal experimental conditions in the following steps: seawater samples were taken and added into silica tubes, 2 mM $NaHCO_3$ was added, pH 8.3 was adjusted, and UV ablation was carried out for two hours, to destroy the organic matter and to convert all the Se (VI) into Se (IV). Then, perchloric acid was added to all the samples to adjust their pH to 2.0, then the determination was carried out. The results were compared with the AFS, as shown in Table 2. In addition, Se (IV) was determined in real seawater samples from the coast using the standard addition method, and the recoveries of the real samples were all in the range of 94–102%. The results are shown in Table 3, which indicates that the developed electrochemical sensing system has good reliability, and can be used for field determination and analysis.

Table 2. Comparison of portable electrochemical system and AFS for the determination of TDSe in real samples (n = 3).

Sample	Proposed Method (µg/L)	AFS (µg/L)
Sample 1	0.19 ± 0.01	0.18
Sample 2	0.22 ± 0.01	0.21
Sample 3	3.25 ± 0.08	3.21

Table 3. Portable electrochemical system for the determination of Se (IV) in real samples (*n* = 3).

Sample	Se (IV) Added (μg/L)	Proposed Method (μg/L)	Recovery (%)
Sample 1	0	0.12 ± 0.01	-
	0.5	0.58 ± 0.02	94
Sample 2	0	0.11 ± 0.01	-
	0.5	0.62 ± 0.01	102
Sample 3	0	1.69 ± 0.04	-
	0.5	2.12 ± 0.06	97

3.6. Field Determination

Based on the above method, field determination of Se (IV) was carried out in Yantai Sishili Bay, Shengshan Island and Zhelin Bay using the developed portable electrochemical systems. The station locations are shown in Figure 6. The concentration content is shown in Figure 7. The Se (IV) concentrations in Yantai Sishili Bay ranged from 0.16–3.59 μg/L (average 1.43 μg/L); the Se (IV) concentrations in Island ranged from 0.20–5.18 μg/L (average 2.06 μg/L); the Se (IV) concentrations in Zhelin Bay ranged from 0.87–4.87 μg/L (average 3.13 μg/L). The average content of Se (IV) in surface seawater was in the order of Zhelin Bay > Shengshan Island > Sishili Bay. The Se (IV) concentration showed an increasing trend from the north to the south of China.

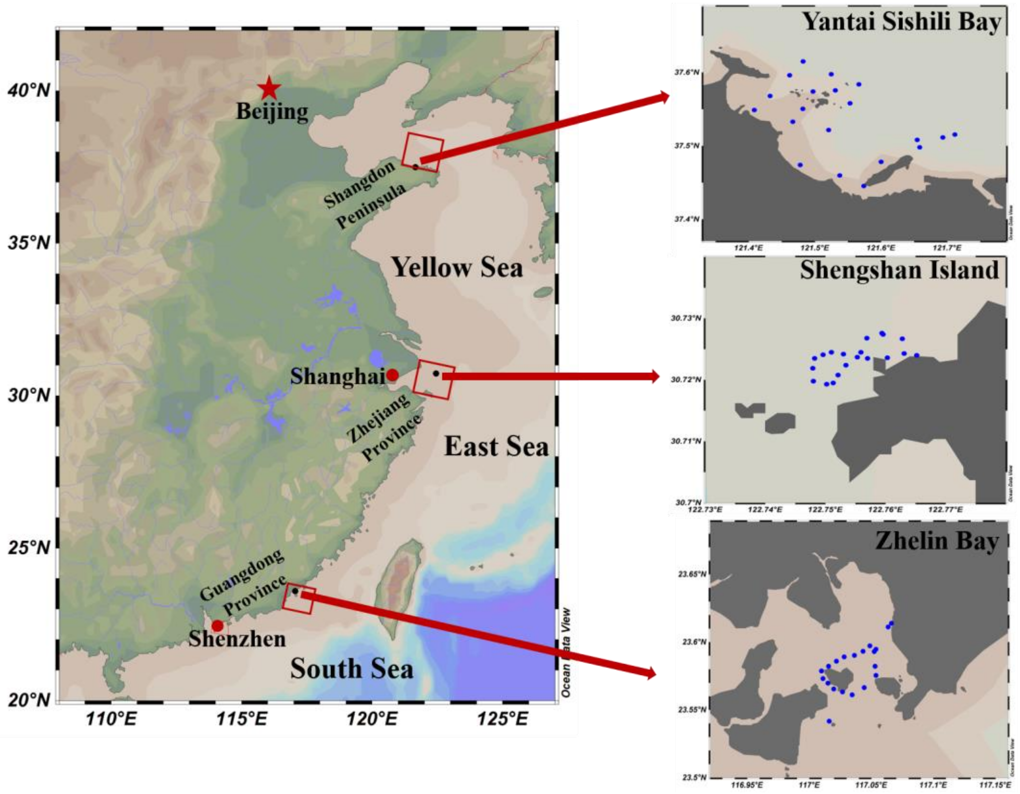

Figure 6. Station locations for testing in Yantai Sishili Bay, Shengshan Island and Zhelin Bay.

Compared with the Se (IV) reported from the world's coastal areas, the average Se (IV) concentrations in the three regions of Yantai Sishili Bay, Shengshan Island, and Zhelin Bay in this study were higher than those in San Francisco Bay (0.01 μg/L) [44], the North Pacific Ocean (0.01 μg/L) [45], the South China Sea (0.04 μg/L) [46], the Atlantic Ocean (0.03 μg/L) [5], and the Mediterranean Sea (0.13 μg/L) [47], but lower than the Arabian Gulf (48.15 μg/L) [48]. Since the sampling sites of Yantai Sishili Bay, Shengshan Island, and Zhelin Bay are located in harbors and near aquaculture areas under the drastic influence of man-made activities in the surrounding area, the concentration is high, but the concentration of Fan is still within the permissible threshold.

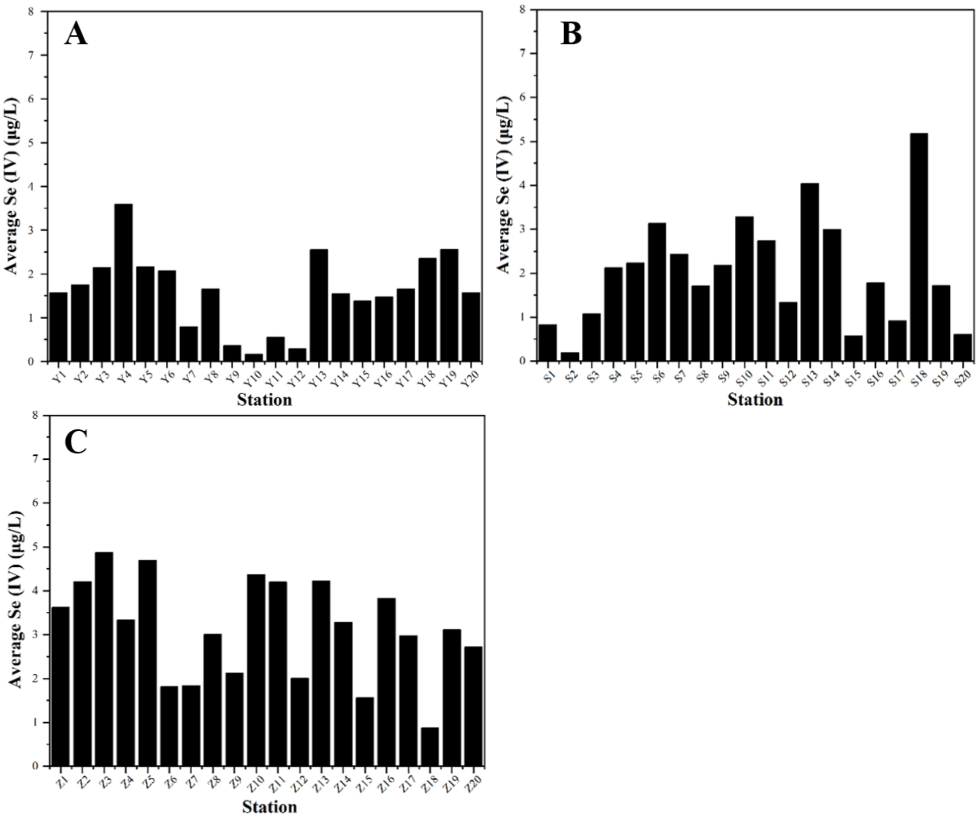

Figure 7. Histograms of average Se (IV) content in Yantai Sishili Bay (**A**), Shengshan Island (**B**) and Zhelin Bay (**C**) ($n = 3$).

4. Conclusions

A novel and effective portable electrochemical system was prepared for the determination of Se (IV) in the coastal seawater of China (North Yellow Sea, East China Sea and South China Sea). The use of excellent catalytic and conductive properties of the rGO/AuNPs/Nafion benefited from the AuNPs, and the increased specific surface area was thanks to the rGO and the protective effect of Nafion. The peak current of the system increases linearly with Se (IV) concentrations from 0.1–30 μg/L, with a determination limit of 0.03 μg/L, and the determination limit is much lower than the limit value allowed by the World Health Organization. In addition, the repeatability and reproducibility of the electrodes support their candidacy for the economic analysis of selenium in seawater. Although many methods have been reported for the determination of selenium in water, most of them are stuck in laboratory tests. The portable electrochemical analyzer proposed in this paper has been successfully used to achieve rapid determination and analysis in the field due to its reliability and fast analytical speed. However, it is still difficult to commercialize on a large scale. In the future, the portable electrochemical sensing system developed by us will not only be applied to the field detection of Se (IV) in seawater, but will also be further extended to the field detection of Se (IV) for the microbiological content determination, or in other environmental conditions (e.g., acid mine drainage, freshwater, etc.). The development of this system will hopefully be able to provide a good platform for water quality assessment and collaboration in more research areas. In addition, this portable electrochemical system can be further developed, and is expected to enable offline automated monitoring without human intervention.

Author Contributions: Conceptualization, methodology, software, validation, formal analysis, investigation, data curation, writing—original draft preparation, T.L.; conceptualization, resources, supervision, project administration, funding acquisition, writing—review & editing, D.P.; methodology, writing—review & editing, H.W.; writing—review & editing, Y.L. (Ying Li), M.A.R. and Y.L. (Yan Liang). All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by Key R&D Program of Shandong Province, China (2022CXPT019), the Strategic Priority Research Program (XDB42000000) of Chinese Academy of Sciences, the Taishan Scholar Project of Shandong Province (tsqn202103133), Science & Technology Specific Projects in Agricultural High-tech Industrial Demonstration Area of the Yellow River Delta (2022SZX01) and the Special Fund for the Scholar Program of Yantai City.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data is contained within the article.

Conflicts of Interest: Author Dawei Pan works part-time in Shandong Saline-Alkali Land Modern Agriculture Company for saline water quality monitoring, where the research work and equipment could be applied in the future. The remaining authors declare that this study was conducted without any business or financial relationship that could be considered as a potential conflict of interest.

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