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An anodic stripping voltammetric approach for total mercury determination in sea sponges from the Niger Delta region of Nigeria

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ABSTRACT

Mercury pollution from ongoing crude oil refining and waste disposal activities threatens aquatic ecosystems and human health in the Niger Delta. Mercury monitoring exercise in this region is challenging due to the high cost of traditional instruments and the complexity of marine samples. This research presents a novel analytical method using differential pulse anodic stripping voltammetry (DPASV) with a glassy carbon electrode (GCE) to determine mercury levels in sea sponges from the Niger Delta. Using a 2.36 M HCl + 2.4 M NaCl supporting electrolyte, −0.6 V deposition potential, and 300 s deposition time, average mercury levels were found to be 0.98 mg kg^{-1}, 0.63 mg kg^{-1} and 0.42 mg kg^{-1} for Ibiotirem, Kaa and Samanga, respectively. The result showed that the Niger Delta is polluted, and remediation efforts are necessary. Furthermore, the DPASV method could be used for routine mercury monitoring as it is cost-effective, user-friendly, and highly sensitive.

1. Introduction

The presence of mercury in the environment is widespread, and is thought to have substantial toxicological consequences for both aquatic systems and human health (Wang et al., 2021; Gojkovic et al., 2023). The global concern relating to mercury contamination arises from its persistence, bio-accumulative characteristics, and capacity to biomagnify throughout the food chain (Saidon et al., 2024). Anthropogenic activities such as industrial processes and fossil fuel combustion are primary sources of mercury emissions, leading to widespread contamination of aquatic ecosystems (Charvát et al., 2020; Jung et al., 2021). In marine environments, mercury contamination can have harmful effects on aquatic organisms, ecosystem dynamics, and human populations dependent on seafood for sustenance. From bioaccumulation in marine species to disruptions in reproduction and development, as well as the broader consequences relating to ecosystem functioning and human health, the impacts of mercury contamination highlight the urgent need for comprehensive mitigation measures (Hilgendag et al., 2022; Basu et al., 2023).

The Niger Delta, located in southern Nigeria (Fig. 1), is one of the world's largest and most biodiverse deltaic regions, renowned for its rich aquatic resources and mangrove ecosystems (Elekwachi et al., 2021; Uwadiae et al., 2023). However, extensive oil and gas exploration, urbanisation, and industrial activities in the region have led to severe environmental degradation, including widespread pollution of water bodies with potentially toxic metals, including mercury (Umeoguaju et al., 2022; Numbere et al., 2023). Achudume (Achudume, 2009) reported an elevated mercury concentration of 4.24 μg l^{-1} in water from the Niger Delta. Otitoju and Otitoju (Otitoju and Otitoju, 2013) reported a mercury concentration of 6.42 mg kg^{-1} in snail (*Tympanotonus fuscastus*) from the Niger Delta. Furthermore, Anyanwu *et al.* (Anyanwu et al., 2023) also reported that water samples from the Niger Delta were highly contaminated with mercury, with a contamination factor ranging between 3.48 and 44.48. Thus, the Niger Delta is thus considered a hotspot for mercury contamination, with adverse consequences for both the environment and public health (Anyanwu et al., 2023; Olufemi et al., 2020).

Sea sponges are sessile filter-feeding organisms found in marine ecosystems, known for their ability to accumulate metals from their surrounding (Krikech et al., 2022; Maggioni et al., 2024). Due to their mode of feeding and lifestyle, sea sponges can accumulate metals from seawater and sediments in their tissues over time (Akpiri et al., 2020). Measuring levels of metals in sea sponge tissues could help provide understanding into the extent of metal contamination in their environment (Vidyalakshmi et al., 2024). Thus, sea sponges could be biomonitors of metal contamination in marine environments. Humans do not directly consume sea sponges. However, through bioaccumulation and biomagnification, sea sponges can give understanding into the

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potential risks to commercially important species, such as fish, which can ultimately impact the Niger Delta population dependent on seafood for sustenance. Despite their ecological importance, there is no study on mercury accumulation in sea sponges from the Niger Delta.

Furthermore, the few studies that have successfully measured metal levels in sea sponges from other parts of the world have used various instruments, including Direct Mercury Analyzer (Roveta et al., 2020), Inductively coupled plasma mass spectrometry (ICP-MS) (Krikech et al., 2022), and Atomic Absorption Spectrometry (AAS) (Pan et al., 2011). Unfortunately, these instruments come with selectivity challenges, meaning they may not be able to accurately distinguish between different metals present in complex environmental samples. Moreover, operating these instruments often requires specialised training and expertise, adding to the complexity and cost of metal analysis. The high initial investment and maintenance costs associated with these instruments further limit their accessibility, particularly for researchers and institutions with limited resources. Thus, the case for an alternative method, such as anodic stripping voltammetry (ASV), in determining total mercury levels in sea sponges.

ASV is an electrochemical technique widely used for trace metal analysis due to its low cost, high sensitivity, low detection limits, and rapid analysis time (Honeychurch et al., 2018; Honeychurch, 2019; Nguyen et al., 2021). ASV involves the deposition of the target metal onto an electrode surface followed by its stripping through anodic potential scanning, allowing for quantitative determination of the analyte concentration (Xu et al., 2021; Bambuwu, 2023) While ASV has been employed for mercury determination in various matrices, its application to marine invertebrates, specifically sea sponges, remains novel to this study.

This study aims to develop an ASV approach for the determination of total mercury levels in sea sponges collected from different sites within the Niger Delta. The objectives of this study are to (1) assess mercury contamination levels in sea sponges from the Niger Delta, (2) validate the proposed ASV method against a conventional analytical technique (Inductively coupled plasma-optical emission spectrometry (ICP-OES)), and (3) discuss the implications of the findings for environmental management and conservation in the region.

2. Materials and methods

2.1. Study area

The Niger Delta region, located in southern Nigeria, is comprised of nine states (Fig. 1). The area is characterised by a network of rivers, creeks, and mangrove swamps that form a vast delta where the Niger River empties into the Gulf of Guinea. Additionally, it is a rich and biodiverse ecosystem. While it is challenging to provide an accurate account due to ongoing research and discoveries, the region is home to a wide variety of flora and fauna.

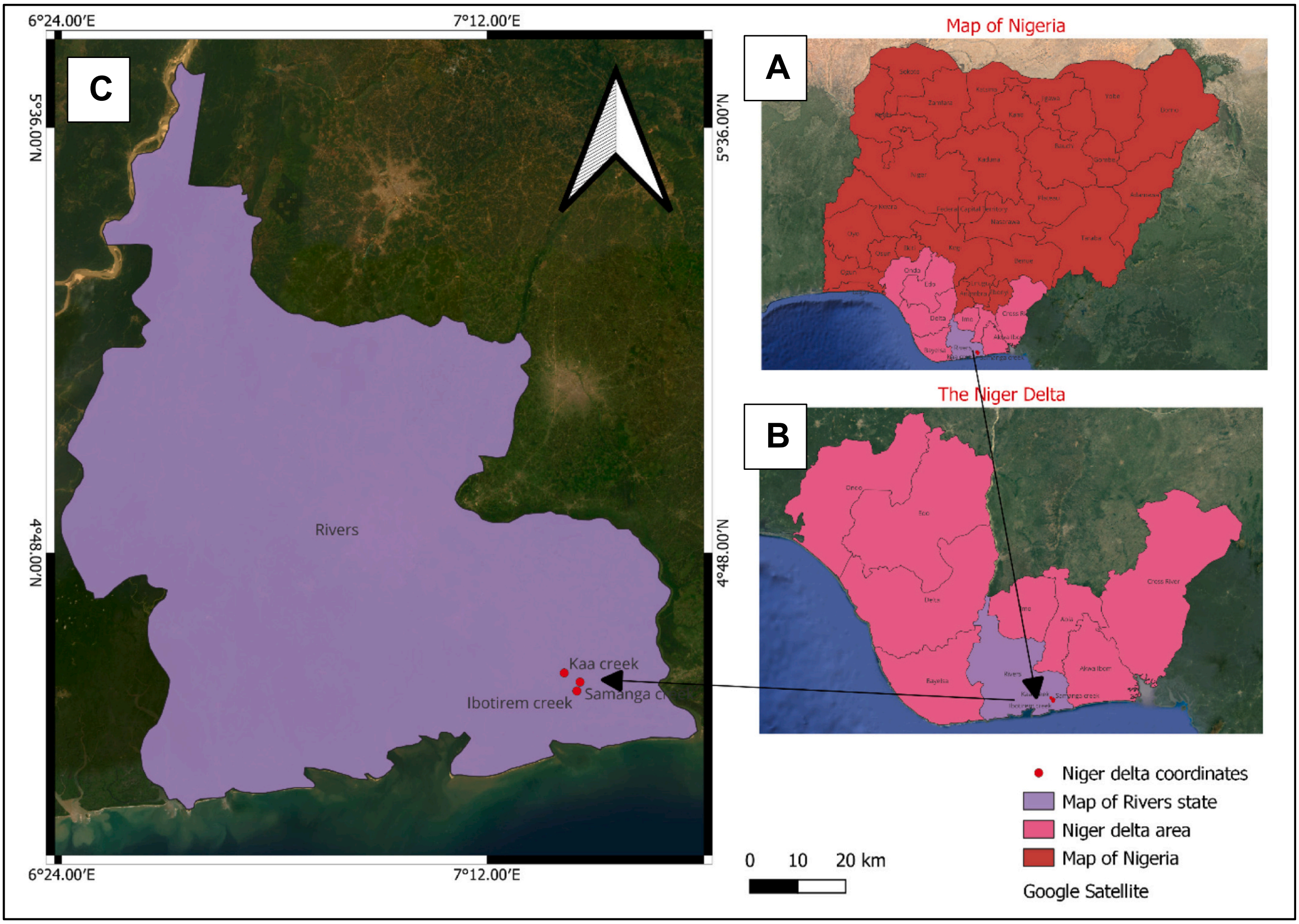

Fig. 1. (A) A map of Nigeria highlighting the Niger Delta area (B) Map of the Niger Delta highlighting the area of the Niger Delta where samples were collected (C) An administrative map of Rivers state showing sample locations in red dots. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2.2. Chemicals and reagents

All chemicals were analytical grade and supplied from Fisher Scientific, Loughborough, UK. Working mercury solutions were prepared by diluting a mercury stock solution (1000 ppm) in 2.36 M hydrochloric acid. All acids and buffer solutions used for supporting electrolyte optimisation studies were prepared by diluting the appropriate volume of the pure compound in deionised water to give a 2.36 M solution. Sodium acetate buffer was prepared by stepwise adjustment of a 2.36 M acetic acid solution with 2.36 M sodium acetate to give a pH 3.1 solution. A sodium chloride solution of 2.4 M was also prepared. All supporting electrolytes were freshly prepared on the day of use.

2.3. Sea sponge collection and processing

Sea sponge *Amorphinopsis* sp. samples (Fig. 2) were collected from three sites (Table 1) in the Niger Delta area of Nigeria on exposed mangrove stumps and hard surfaces at low tide using sterile scalpels samples were placed in sealed plastic bags containing seawater and transported to the laboratory. In the laboratory, following the method of Akpiri (Akpiri, 2018), sponge tissues were washed three times in seawater to remove debris and stored at −20 °C until use.

Furthermore, sponge tissues were freeze-dried using Thermo Fisher's Heto PowerDry PL3000 Freeze Dryer (Loughborough, UK) and homogenised using a mortar and pestle. A 2 g sponge tissue sample was digested with 10 ml of 11.8 M hydrochloric acid (HCL) in a MARS 6 microwave vessel (CEM corporation, Buckingham Industrial Park, UK). The process was repeated a second time to ensure total digestion. After completing the digestion process, the vessel was allowed to cool. The content of the vessel was then filtered using a Grade 541 Whatman filter paper into a 50 ml volumetric flask and made up to 50 ml with deionised water.

The concentrations of Mercury in sponge tissues expressed as dry weight were calculated using the following equation:

$$C\left(mg\cdot kg^{-1}\right)=\frac{c_{ob}\left(mg\cdot l^{-1}\right)\times k\times V\left(l\right)}{a\left(kg\right)} \tag{1}$$

where c_{ob} is the concentration observed in the sponge digest, V is the volume of sponge digest, k is the dilution factor, and a is the mass of the sponge tissue sample.

Table 1
Sampling sites in the Niger Delta area of Nigeria.

Sites	Site name	Geographical coordinates
S1	Kaa creek	4°34′26.4″N 7°20′45.4″E
S2	Samanga creek	4°33′25.0″N 7°22′32.7″E
S3	Ibotirem creek	4°32′24.4″N 7°22′11.1″E

2.4. Apparatus and instrumentation

Cyclic voltammetry and differential pulse anodic stripping voltammetry (DPASV) were carried out using an EmsStat^3 potentiostat linked to a PC for data acquisition using the PSTrace 4 software version 4.8.7 (PalmSens, Houten, The Netherlands). A voltammetric cell comprising of a 3 mm diameter glassy carbon working electrode (GCE), an Ag/AgCl reference electrode in a 3.0 M KCl solution, and a platinum wire counter-electrode. Before use, the GCE was manually polished on a polishing mat modified with an aqueous slurry of 5 μm aluminium oxide. The GCE was then rinsed with deionised water and dried with a tissue. The electrodes were connected to the potentiostat (Ivium, Eindhoven, The Netherlands), connected to a computer with an electrochemical system software package, Ivium software Windows 10 version, for data acquisition and control. A small magnetic stirrer disc was put at the bottom of the cell for stirring during the preconcentration step of DPASV, which revolved at a predetermined consistent rate by a magnetic stirrer. The electrochemical cell comprised a 5 ml sample in 2.36 M HCl and 5 ml 2.4 M NaCl.

The Agilent 5110 inductively coupled plasma-optical emission spectrometer (ICP-OES) (Agilent Technologies, Santa Clara, United States) was used. The instrument was equipped with a SeaSpray nebuliser, double-pass cyclonic spray chamber, 1.2 mm i.d Alumina injector, and a Standard quartz torch. The instrument operating parameters are shown in Table 2.

Fig. 2. Freshly collected *Amorphinopsis* sp.

Table 2
Instrument parameters for ICP-OES Agilent 5110.

View	Axial view
Optical system	Echelle
Detector	Solid state detector
Power/W	1300
Plasma flow (L/min)	15
Auxiliary flow (L/min)	0.5
Sample flow rate/ml min^{-1}	0.8

2.5. Voltammetric procedures

Cyclic voltammograms were initially recorded in various supporting electrolytes. Cyclic voltammetric investigations were undertaken using a starting potential of +0.5 V and a switching potential of −1.0 V. at a scan rate of 50 mVs^{-1}. Anodic stripping voltammetry (ASV) was carried out using a differential pulse waveform. The deposition was carried out for 300 s at −0.6 V (vs Ag/AgCl/KCl) while stirring the solution using a magnetic stirrer bar. Following deposition, the stirring was stopped, and the stripping voltammogram was recorded from −0.6 V to +0.5 V using a pulse amplitude of 50 mV, step height of 10 mV, pulse width of 50 ms, and step width of 0.5 s.

2.6. Method evaluation

Following optimisation studies, the analytical performance characteristics of the optimised method were validated. The linear range, limit of detection, limit of quantification and percentage recovery were evaluated. The effect of concentration was investigated over the mercury concentration range of 2 ppb to 25 ppb ($n = 5$). All measurements were undertaken in triplicate. The sensitivity of the working electrode was determined using the equation below.

$$\text{Sensitivity} = \frac{Slope\ (from\ calibration\ plot)}{Active\ surface\ area\ of\ electrode} \tag{2}$$

Sample mercury concentrations were determined using multiple standard additions. The recovery was determined by spiking freeze-dried and homogenised sea sponge tissue with 0.075 mg kg^{-1} Hg. The recovery was calculated using the equation below.

$$Recovery = \frac{C_y - C_x}{C_z} \times 100 \tag{3}$$

where:

$\boldsymbol{C_y}$ = The concentration of mercury found after the addition of the standard solution
$\boldsymbol{C_x}$ = The concentration of mercury found before the addition of the standard solution
$\boldsymbol{C_z}$ = Concentration of mercury standard added in the sample.

2.7. Method validation

To verify the accuracy of the developed ASV method, samples processed in Section 2.3 were analysed for total mercury using the Agilent 5900 ICP-OES (United States). To compare the results obtained from ASV and ICP-OES, a one-tailed paired *t*-test was used to test if there were statistically significant differences between DPASV and ICP-OES (Huson, 2003).

The paired t-value was subsequently calculated.

$$t_{cal} = \frac{(\overline{d})\sqrt{n}}{S_d} \tag{4}$$

where $\overline{d}$ is the mean of the difference between the two results using the formula:

$$\overline{d} = \frac{\sum_{i=1}^{n} d_i}{n} \tag{5}$$

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

$$S_d = \sqrt{\frac{\sum (d_i - \overline{d})^2}{n-1}} \tag{6}$$

3. Results

3.1. Cyclic voltammetric behaviour

3.1.1. Effect of supporting electrolyte

Initial studies were conducted on a wide range of supporting electrolytes to optimise the conditions for the electrochemical determination of Hg^{2+} using the GCE. Cyclic voltammograms obtained for 20 mg/l Hg^{2+} in a variety of supporting electrolytes (all at 2.36 M) are shown in Fig. 3.

3.1.2. Effect of sodium chloride concentration on Hg^{2+} peak height

3.2. Differential pulse anodic stripping voltammetry

3.2.1. Effect of deposition potential

3.2.2. Effect of deposition time

3.2.3. Calibration curve and limit of detection

Using a deposition potential of −0.6 V and deposition time of 300 s, a linear relationship between Hg^{2+} and i_{pa} (μA) was obtained over 2 ng/ml and 25 ng/ml. The straight-line equation was $i_{pa}(\mu A) = 0.9358x - 0.0669$; ($R^2 = 0.999$ and $n = 5$)

- The detection limit (LOD) is calculated from the calibration curve as follows:

$LOD = \frac{K\sigma}{S}$ where $K = 3$; σ = standard deviation and S = slope of the calibration curve.

LOD for Hg^{2+} is = 0.66 μg l^{-1}

- The quantitation limit (LOQ) was calculated from the calibration curve as follows:

$LOQ = \frac{K\sigma}{S}$ where $K = 10$; σ = standard deviation and S = slope of the calibration curve.

LOQ for Hg^{2+} is = 2.19 μg l^{-1}.

The sensitivity of the electrode was found to be 0.13 μA ppb^{-1} mm^{-2}.

The reproducibility of the method was evaluated by nine repetitive measurements of Hg^{2+}. The Coefficient of Variation (CV) was calculated to be 0.65 % ($n = 5$).

3.3. Application of the method to environmental samples

Levels of Hg^{2+} were measured in sea sponges using the method of multiple additions.

3.4. ASV method using ICP-OES

To validate the results obtained by DPASV, sea sponge samples were

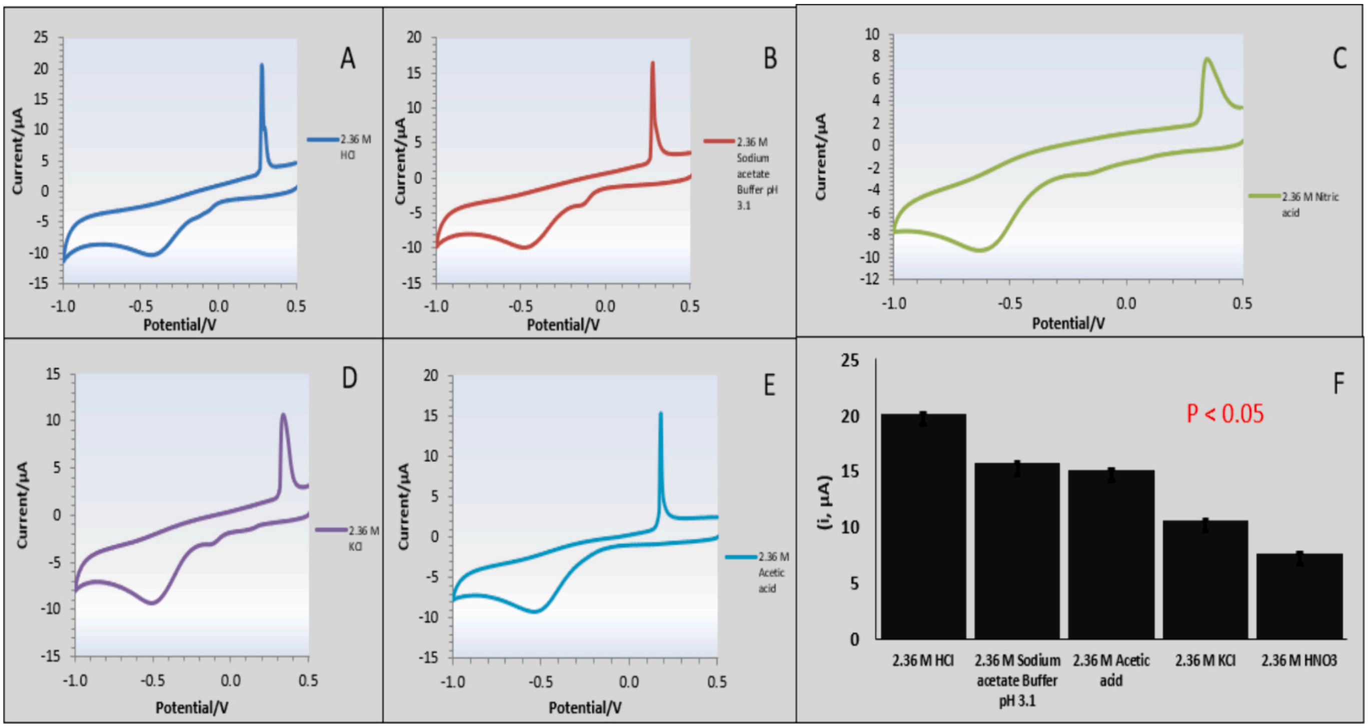

Fig. 3. A–E. Cyclic voltammograms obtained with a glassy carbon electrode for a variety of supporting electrolytes (all at 2.36 M) containing 20 mg/l Hg^{2+} (a) HCl (b) sodium acetate buffer pH 3.1 (c) nitric acid (d) potassium chloride (e) acetic acid. Starting potential, +0.5 V; scan rate 50 mVs^{-1} switching potential, −1.0 V. Fig. F: Histogram comparing peak height obtained via Cyclic Voltammetry of supporting electrolyte A–E. One-way ANOVA showed a statistically significant difference $P < 0.05$; $P = 3.59 \times 10^{-52}$. Error bars represent SEM.

also analysed using ICP-OES. The results of Hg^{2+} concentration in sea sponges from ASV and ICP-OES were compared (Table 6).

4. Discussion

4.1. Supporting electrolyte

This study investigated the cyclic voltammetry behaviour of Hg^{2+} in a range of supporting electrolytes. The investigation offers insights into the complex interplay between the GCE surface, Hg^{2+}, and the surrounding electrolyte solution. Overall, it serves a fundamental purpose in understanding the electrochemical properties and interactions of Hg^{2+} within different chemical environments. Fig. 3 F presents a comparison of i_{pa} for 20 mg/l Hg^{2+} obtained in a variety of supporting electrolytes. The resulting voltammograms were characterised by one cathodic peak on the forward scan and a sharp, symmetrical anodic peak on the reverse scan. This latter behaviour is typical of oxidation of a thin film deposited onto an electrode surface (Honeychurch et al., 2000). Such behaviour is necessary for the accumulation step in anodic stripping voltammetry. Therefore, these initial studies indicated the possibility of using this behaviour to determine trace Hg concentrations. The highest i_{pa} which was statistically significant ($P < 0.05$), was observed in 2.36 M HCl. Therefore, this electrolyte was chosen for further studies involving DPASV. The use of HCl as an excellent supporting electrolyte was also demonstrated by Nguyen et al. (Nguyen et al., 2021).

Salinity levels in environmental samples, such as sea sponges, can significantly affect the kinetics and thermodynamics of the stripping process, potentially leading to inaccurate results if not properly accounted for. Sodium chloride at modest concentrations can increase the efficiency of mercury stripping by enhancing conductivity and promoting the accumulation of Hg^{2+} on the GCE surface. This can lead to more distinct and clearly defined peaks in the stripping process, as well as enhanced sensitivity in the detection of mercury. Excessive quantities of NaCl can cause ion association effects, elevated background currents, and interference with the stripping process, ultimately compromising the accuracy and repeatability of mercury determination. Figs. 4 and 5 show that the mercury stripping peak was well-defined when 5 ml of 2.4 M NaCl was added to the electrochemical cell. However, as the concentration was increased further, the stripping peak was reduced, thus supporting the previous argument. From Fig. 6, the addition of 2.4 M NaCl increases the efficiency of the mercury stripping step. Hence, it is crucial to meticulously optimise NaCl concentration to balance the advantages of enhanced electrochemical performance and potential disadvantages such as interference and signal-to-noise ratio problems.

4.2. Effect of the DPASV parameters

4.2.1. Deposition potential

In this paper, the interest was to develop a quick, sensitive, and selective method for determining trace levels of Hg^{2+} in sea sponges. Therefore, the differential pulse DPASV was used (Manikandan et al., 2023; Zhang et al., 2023). The sensitivity of DPASV relies on deposition potential and deposition time (Nguyen et al., 2021; Ghalkhani et al., 2018). The effect of deposition potential on the Hg^{2+} stripping peak was investigated over −1.0 V to 0.5 V for 50 ng/ml mercury. Fig. 7 shows that the mercury stripping peak was dependent on the deposition potential. The highest value of the mercury stripping peak was obtained at a deposition potential of −0.6 V. After that, the stripping peak decreased when the deposition potential was increased from −0.5 V to 0.5 V. Hence, the deposition potential of −0.6 V was used in further measurements.

4.2.2. Deposition time

The effect of deposition time was investigated over the range of 60 s to 480 s using 50 ng/ml mercury in 2.36 M HCl and 2.4 M NaCl. From Fig. 8, the mercury stripping peak increased as deposition time was increased from 60 s to 300 s. After 300 s, the mercury stripping peak

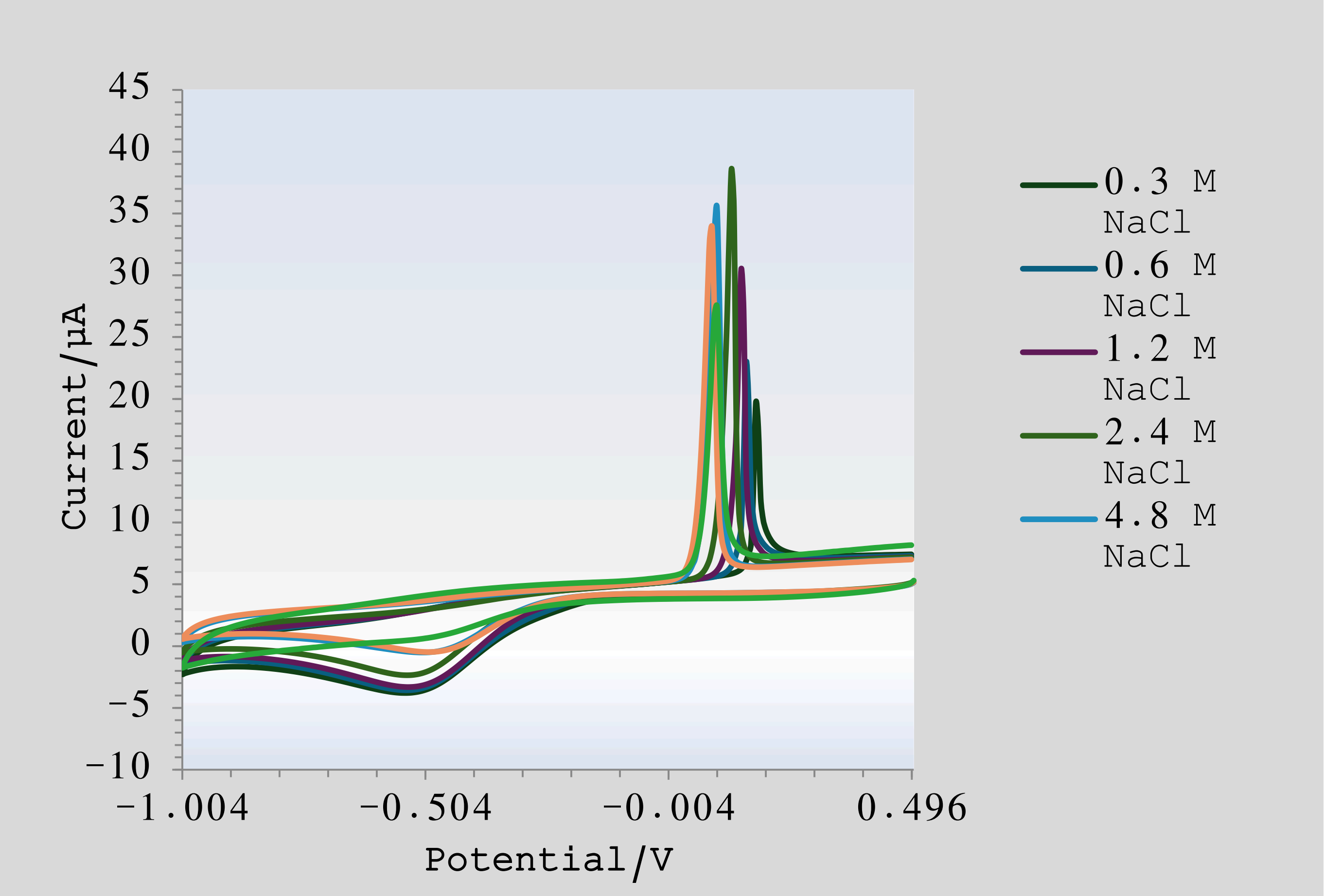

Fig. 4. Cyclic voltammetric behaviour of 20 mg/l Hg^{2+} In 2.36 M HCl in the presence of varying concentrations of NaCl. Starting potential, +0.5 V; scan rate 50 mVs^{-1} switching potential, −1.0 V. The highest stripping peak was observed in 2.4 M NaCl.

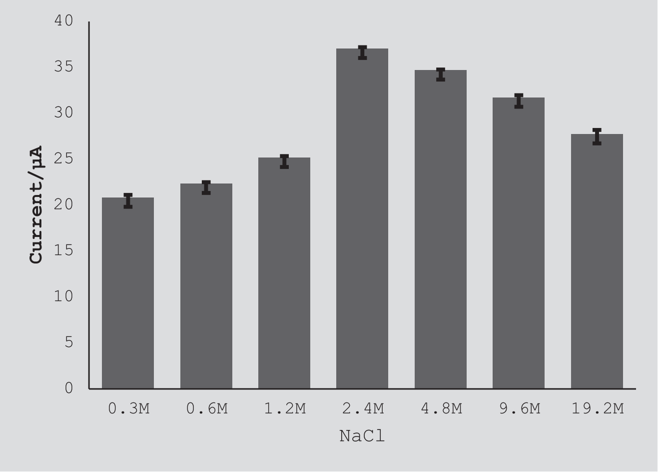

Fig. 5. Histogram comparing peak height obtained via Cyclic Voltammetry of supporting electrolyte in the Presence of 0.3 M NaCl – 19.2 M NaCl. Error bars represent SEM.

plateaued, indicating that the GCE was saturated. Therefore, a 300 s deposition potential was chosen for depositing 50 ng/ml mercury on the surface of the GCE.

4.3. *Calibration studies/validation of DPASV method*

Calibration studies provided an understanding of the analytical performance of the method for detecting Hg^{2+}. Calculating LOD and LOQ allows the determination of the method's sensitivity and ability to accurately detect low concentrations of Hg2+ in the sample. The calibration curve was obtained over the range of 2 ng/ml and 25 ng/ml mercury using a deposition potential of −0.6 V and a deposition time of 300 s. The LOD and LOQ values from the calibration curve were 0.66 μg l^{-1} and 2.19 μg l^{-1}, respectively. The result indicates that the DPASV method can detect and quantify Hg^{2+} at very low levels with good sensitivity. These values represent the concentrations of Hg^{2+} at which the signal-to-noise ratio is 3:1 and 10:1, respectively, demonstrating the method's ability to distinguish between analyte signals and background noise (María-Hormigos et al., 2016). The low LOD and LOQ values suggest the DPASV method is well-suited for analysing mercury ions at trace levels. This is particularly useful in environmental monitoring and regulatory compliance, where even small mercury concentrations can have significant health and environmental implications.

Furthermore, the evaluation of method reproducibility through repeated measurements of Hg^{2+} demonstrates excellent precision, as indicated by the low Coefficient of Variation (CV) of 0.65 %. This suggests that the DPASV method produces consistent and reliable results across multiple measurements, which is essential for ensuring the accuracy and robustness of analytical data. The method's high reproducibility enhances confidence in the validity of the calibration curve and the accuracy of concentration determinations.

To further validate the results obtained by DPASV, the proposed

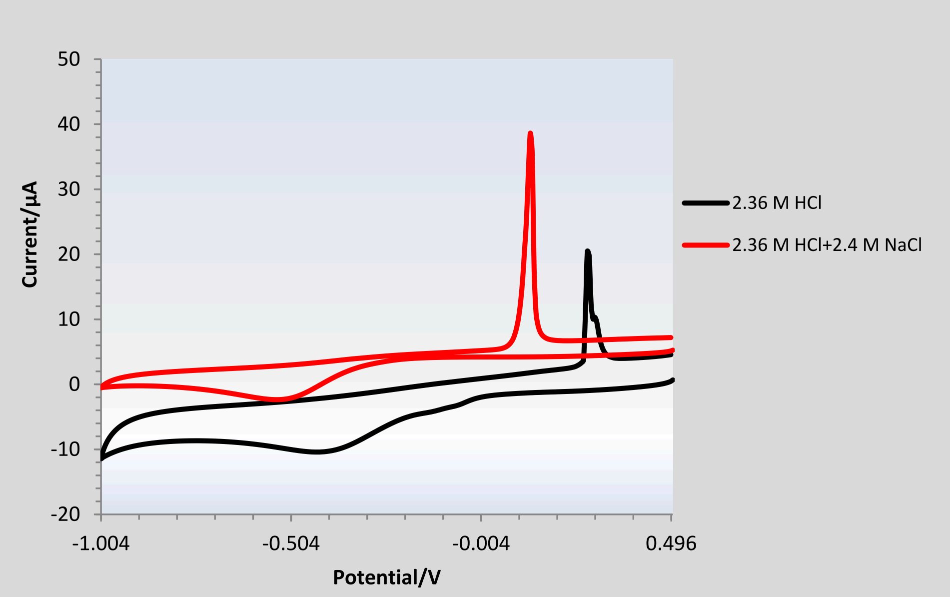

Fig. 6. Cyclic voltammetric behaviour of 20 mg/l Hg^{2+} In 2.36 M HCl in the presence of 2.4 M NaCl and the absence of NaCl. Starting potential, +0.5 V; scan rate 50 mVs^{-1} switching potential, −1.0 V.

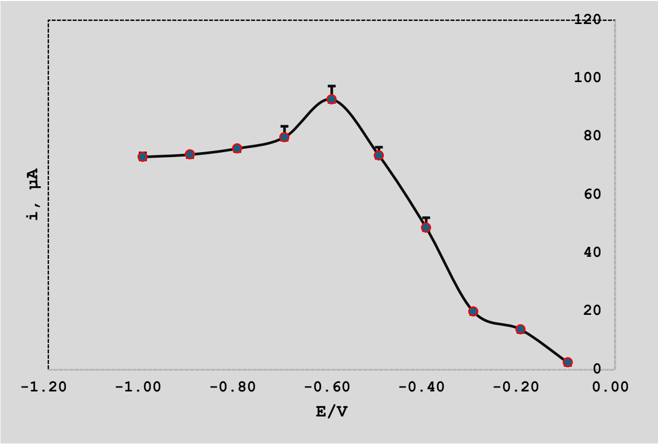

Fig. 7. Effect of deposition potential on the DPASV of Hg^{2+} at 20 mg/l in 2.36 M HCl and 2.4 M NaCl. Deposition time, 60 s, and scan rate 50 mVs^{-1}. Error bars represent SEM.

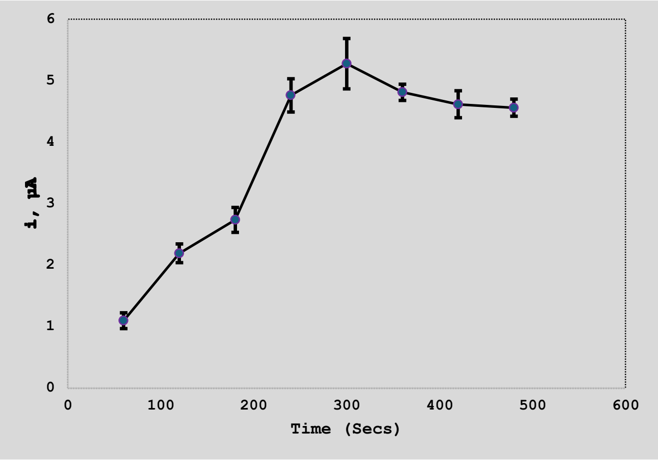

Fig. 8. Effect of deposition time on the DPASV of Hg^{2+} at 20 mg/l in 2.36 M HCl and 2.4 M NaCl. Deposition potential −0.6 V, and scan rate 50 mVs^{-1}. Error bars represent SEM.

method in this paper was compared with those obtained by the ICP-OES method. From Table 5, t_{cal} (1.92) is less than the t_{tab} (2.57) at the 95 % confidence level and 5 degrees of freedom. The result means no statistically significant difference exists between the ASV and ICP-OES methods of quantifying mercury in sea sponges. However, this paper suggests that ASV is better due to its sensitivity, selectivity, low cost, ease of use, and possibility of use on-site. Furthermore, ASV stands out as there is the possibility of modifying the working electrode surface to improve the selectivity to mercury and other metals, as shown by (Fayazi, 2020; Koshki et al., 2021; Fayazi et al., 2022).

4.4. Application of the method to samples

The proposed method was successfully applied to determine mercury concentrations in sea sponges from the Niger Delta region of Nigeria before and after fortifying with Hg^{2+} at concentrations of 0.075 mg kg^{-1} The DPASV parameters were the same as described in Section 2.5. The levels of Hg^{2+} were determined using the method of multiple standard additions (n = 5). Fig. 9 shows the voltammograms obtained for sea sponge samples before and after fortifying with mercury standard. From Tables 3, 4 and 5, the mean recovery for Ibotirem, Samanga and Kaa was found to be 82.10 % ± 5.05 (n = 9), 98.44 % ± 5.89 (n = 9) and 92.01 % ± 3.47 (n = 9), respectively. This novel method revealed that average concentrations of mercury in sponge samples were 0.98 mg kg^{-1}, 0.63 mg kg^{-1} and 0.42 mg kg^{-1} for Ibiotirem, Kaa and Samanga, respectively. Anarado et al. (Anarado et al., 2023) reported slightly higher mercury concentrations than this study in four creeks in Bayelsa state. Otitoju and Otitoju (Otitoju and Otitoju, 2013) also reported a higher mercury concentration of 6.42 mg kg^{-1} in *Tympanotonus fuscastus* from the Niger Delta. This difference in Mercury concentration might be linked to varying proximity to pollution sources (Sultana et al., 2024). No set limit for mercury in sea sponges exists. However, the European Union's Water Framework Directive (WFD) has set the Environmental Quality Standards (EQS) for mercury in marine invertebrates to be 20 ng/g wet weight (≈100 ng/g dry weight) (Gentès et al., 2019). In comparison, the WHO set the maximum permissible limit for mercury in fish to be 500 ng/g (WHO, 1979; Sahebi and Emtyazjoo, 2011). Comparing levels of

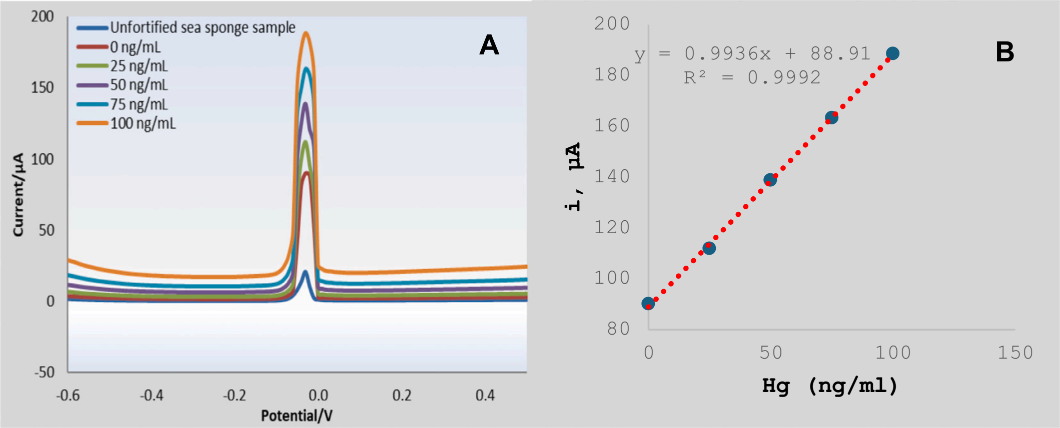

Fig. 9. DPASVs of a representative sea sponge sample unfortified, fortified with 75 ng/g Hg^{2+} and added concentrations of 0 ng/ml Hg^{2+}; 25 ng/ml Hg^{2+}; 50 ng/ml Hg^{2+}; 75 ng/ml Hg^{2+}; 100 ng/ml Hg^{2+} (b) Resulting calibration curve for the fortified sample. Accumulation time: 300 s; Deposition potential: −0.6 V.

Table 3
Recovery and precision data for Hg^{2+} obtained on sea sponge samples from site Ibotirem (mg kg^{-1} dry weight).

Trials	Original sample concentration	Added	Found	Recovery (%)
Trial 1	1.025	0.075	1.085	79.73
	0.950	0.075	1.008	77.20
	0.985	0.075	1.051	87.60
Trial 2	0.860	0.075	0.927	89.73
	0.935	0.075	0.993	77.73
	1.020	0.075	1.082	83.20
Trial 3	1.040	0.075	1.106	88.40
	1.015	0.075	1.071	75.20
	0.945	0.075	1.005	80.13
			Mean %	82.10
			SD	5.05
			CV%	6.15

SD: standard deviation; CV: coefficient of variation.

Table 4
Recovery and precision data for Hg^{2+} obtained on sea sponge samples from site Samanga (mg kg^{-1} dry weight).

Trials	Original sample concentration	Added	Found	Recovery (%)
Trial 1	0.365	0.075	0.439	98.27
	0.460	0.075	0.543	110.80
	0.450	0.075	0.521	94.67
Trial 2	0.350	0.075	0.423	97.20
	0.425	0.075	0.496	94.00
	0.370	0.075	0.448	103.47
Trial 3	0.475	0.075	0.542	88.67
	0.400	0.075	0.474	98.80
	0.450	0.075	0.525	100.13
			Mean %	98.44
			SD	5.89
			CV%	5.98

SD: standard deviation; CV: coefficient of variation.

Table 5
Recovery and precision data for Hg^{2+} obtained on sea sponge samples from site Kaa (mg kg^{-1} dry weight).

Trials	Original sample concentration	Added	Found	Recovery (%)
Trial 1	0.610	0.075	0.678	90.40
	0.730	0.075	0.795	87.20
	0.600	0.075	0.670	93.33
Trial 2	0.720	0.075	0.786	87.60
	0.650	0.075	0.717	89.33
	0.590	0.075	0.663	97.60
Trial 3	0.525	0.075	0.596	94.00
	0.690	0.075	0.762	96.40
	0.540	0.075	0.609	92.27
			Mean %	92.01
			SD	3.47
			CV%	3.78

SD: standard deviation; CV: coefficient of variation.

Table 6
Result of analysis of sea sponge samples in Ibiotirem obtained by ASV and ICP-OES.

Trials	ASV (mg kg^{-1})	ICP-OES (mg kg^{-1})	*d*
Trial 1	1.03	1.01	−0.02
	0.95	1.00	0.05
Trial 2	0.93	1.02	0.08
	1.02	1.03	0.01
Trial 3	1.02	1.46	0.45
	0.94	1.29	0.35
		Mean	0.15
		SD	0.18
$t_{\text{calculated}}$			1.92
t_{table}			2.57

Mercury found in the Niger Delta with limits set by WFD and WHO, the results from this research shows that concentrations of mercury in the Niger Delta are still above permissible limits.

The result suggests that mercury levels in the Niger Delta pose an immediate risk to human health through seafood consumption. Studies have shown that mercury can cause several issues in adults, including disruption of fine motor function, decreased muscular strength, decrease in fertility rate in both males and females, the birth of abnormal offspring, reduction of overall immunity of the body (Zahir et al., 2005; Carocci et al., 2014; Bjørklund et al., 2019; Henriques et al., 2019). In children, low-dose mercury can cause late talking, late walking and autism (Zahir et al., 2005; Yassa, 2014).

The absence of a set limit for mercury for sea sponges indicates a gap in regulatory standards, especially considering their sessile nature, which makes them more susceptible to accumulating contaminants from their surrounding environment. Therefore, there is a need for further research and the establishment of specific guidelines or regulations for mercury levels in sea sponges, as they are integral components of marine ecosystems and potential indicators of environmental health. Overall, this paper puts forward the need for remediation and continued monitoring of mercury levels in the Niger Delta using sea sponges to ensure the protection of both ecosystems and human health.

5. Conclusion

A DPASV method using the glassy carbon electrode (GCE) for determining total mercury in sea sponges from the Niger Delta region of Nigeria has been developed. A 2.36 M HCl + 2.4 M NaCl supporting electrolyte, −0.6 V deposition potential and 300 s deposition time yielded optimal results for determining mercury. The proposed method in this paper has good sensitivity, selectivity, accuracy, and precision. Comparing the DPASV method in this paper to conventional methods such as ICP-OES revealed no significant difference. Applying the DPASV method to sea sponge samples from the Niger Delta revealed that mercury levels in the Niger Delta were above the maximum permissible limit for mercury set by the WFD and WHO. Finally, this paper puts forward sea sponges as excellent bio-monitors of marine pollution.

CRediT authorship contribution statement

N.U. Sunday: Writing – original draft, Methodology, Investigation, Formal analysis, Conceptualization. **K.C. Honeychurch:** Writing – review & editing, Validation, Supervision, Methodology. **L. Newton:** Writing – review & editing, Supervision, Resources. **R.U. Chidugu-Ogborigbo:** Writing – review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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