

# Square Wave Anodic Stripping Voltammetry for Simultaneous Determination of Trace Hg (II) and Tl(I) in Surface Water Samples Using SnO<sub>2</sub>@MWCNTs Modified Glassy Carbon Electrode

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A rapid, simple and sensitive electrochemical sensor based on glassy carbon electrode modified with tin oxide nanoparticles @ multiwalled carbon nanotubes have been used for determination of trace Hg(II) and Tl(I) using the square wave anodic stripping voltammetric (SWASV) technique. Under optimized condition, the limit of detection and quantification ranged from 0.9–1.2 ng L<sup>-1</sup> and 3.3-4.0 ng L<sup>-1</sup>, respectively. The inter-day (n=10) and intra-day (n=7) precisions expressed in relative standard deviations at 50 µg L<sup>-1</sup> of Hg(II) and Tl(I) ranged from 2.1-3.5 and 3.0-4.3%, respectively. The GCE/SnO<sub>2</sub>@MWCNTs was applied for the determination of the target trace elements in thirteen surface water samples. The accuracy of analytical results obtained using the developed electrochemical sensor was comparable to those obtained by the ICP-MS.

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**Keywords:** Tin dioxide@multiwall carbon nanotubes; thallium (I); mercury (II), square wave anodic stripping voltammetry, surface water

## 1. INTRODUCTION

The extensive use of trace metals in many industrial and agricultural activities calls for rapid monitoring and quantification of these elements in the environment. This is because the presence of toxic elements. For instance, thallium (Tl) is the most toxic metal and its toxicity is similar to that of Hg, Cd and Pb [1]. Thallium, like other toxic trace metals, is potentially carcinogenic because it has an ability to cause polymorphism in genes [1-3]. In addition, its compounds are poisonous to living organisms [2]. In general, Tl exist at very low concentrations (below the ng L<sup>-1</sup> level) in most

environmental samples [3]. However, natural processes, processing of ores and industrial applications can introduce thallium into the environment, thus elevating its background concentration [4]. Similar to Tl, mercury (Hg) is highly toxic to human health, and it occurs naturally in the earth's crust. It is released into the environment as a result of human activity and natural processes [5]. Elemental and methyl Hg are toxic to the central and peripheral nervous systems. The inhalation of Hg vapour can produce harmful effects on the nervous, digestive and immune systems, lungs and kidneys, and may be fatal [6].

Monitoring and measuring Hg and Tl in the environment is therefore of great importance. Consequently, there is still an increasing need for sensitive, reliable and robust analytical techniques to measure trace levels of these elements. Traditionally, Hg and Tl quantification is carried out using relatively sensitive techniques. These include cold vapor atomic absorption spectrometry [7], inductively coupled plasma optical emission spectrometry (ICP-OES) [8], inductively coupled plasma-mass spectrometry (ICP-MS) [9], X-ray fluorescence spectrometry (XRF) [10] and graphite furnace atomic absorption spectrometry (GFAAS) [11]. Although these analytical techniques are the certified methods for trace metal determination and have high accuracy and the lowest detection limits, they are sophisticated and require highly skilled personnel [12]. They also require sample preparation before analysis, which is time-consuming and tiresome [13]. In addition, spectrometric techniques are not suitable for speciation (only suitable for total metal determination) and in-situ analysis of metals [14]. Therefore, the aforementioned challenges justify the search for rapid, simple and highly sensitive alternative analytical methods such as stripping based electrochemical techniques with improved limits of detection [15].

Electroanalytical techniques as an alternative of spectrometric methods have been accepted as one of the most efficient tools for accurate quantification of trace metal ions such as Tl and Hg in different sample matrices [16]. This is because electroanalytical methods are simple to operate, sensitive, rapid and use low cost portable and easy to maintain instrumentation [15]. Among all electroanalytical methods, the stripping voltammetry provides a powerful tool for the determination of metal concentrations in environmental matrices. Stripping voltammetry (either cathodic or anodic) possesses high-sensitivity and can simultaneously analyze several trace metal ions [17]. However, when dealing with difficult matrices, leakage in selectivity of a stripping voltammetric procedure becomes a serious challenge [15]. The leakage in sensitivity often occurs when different species in the sample undergo redox reactions at potential values that are very close to each other [15-16]. To overcome this challenge, the use of common experimental handlings such as chemically modified electrodes are recommended. In addition, modified electrodes significantly improve the accumulation efficiency of target analytes [14]. Nanostructured materials are extremely attractive to modify electrodes for electrochemical detection of trace metal ions. This is due to their unique electronic, chemical, thermal, and mechanical properties in comparison with conventional materials [14, 18]. Several researchers have reported the use of different chemical modifiers such as carbon nanotubes [19-23], graphene oxide [24-26], and nanometer sized metal oxides [27-28], nanocomposite of carbon based material mixed with nanometer sized metal oxides [29-31], among others.

Even though numerous articles on electrochemical determination of trace metal ions using modified electrodes have been published, there is still a need for developing more electrochemical

sensing devices. The aim of this work was synthesise tin oxide nanoparticles @ multiwalled carbon nanotubes (SnO<sub>2</sub>@MWCNTs) nanocomposite and apply it to fabricate a electrochemical sensor for the simultaneous determination of Tl (I) and Hg (II) in environmental samples. Square wave anodic stripping voltammetry (SWASV) was used as the electroanalytical detection technique. In this study, SnO<sub>2</sub> nanoparticles (NPs) were selected due its distinctive properties such as high electrical conductivity and chemical sensitivity [14]. Since SnO<sub>2</sub> NPs agglomerates easily (thus affecting their electrochemical performance), MWCNTs was used as a support. MWCNTs were chosen because of their unique properties which include high surface area, chemical stability and high electrical conductivity, among others [32]. To the best of our knowledge it is the first time SnO<sub>2</sub>@MWCNTs nanocomposite is reported for simultaneous determination and Tl (I) and Hg (II) the combination of the two nanomaterials led to a highly sensitive electrochemical sensor. The optimization of factors affecting the electrochemical detection of Tl (I) and Hg (II) was achieved by full factorial design.

## 2. EXPERIMENTAL

### 2.1 Reagents and Materials

All other reagents and chemicals were of analytical reagent grade and doubly distilled water was used in experiments. high purity multiwall carbon nanotubes (MWCNTs, >95% purity), ethanol, sulphuric acid, sodium acetate, glacial acetic acid, hexacyanoferrate, cetyltrimethylammonium bromide (CTAB), sodium hydroxide N,N-dimethylformamide (DMF) were obtained from Sigma-Aldrich (Bellefonte, PA, USA). Standard stock solutions of Tl and Hg (1000 mg L<sup>-1</sup>, atomic absorption standard solutions) were obtained from Sigma-Aldrich. Acetate buffer (1.0 mol L<sup>-1</sup>) was used as a supporting electrolyte.

### 2.2 Instrumentation

Electrochemical measurement, cyclic voltammetry (CV), were performed using a  $\mu$ -Autolab TYPE III and driven by the NOVA software (Version 1.8) in conjunction with a conventional three-electrode system and a personal computer for data storage and processing. A modified glassy carbon electrode employed as the working electrode and a platinum wire as the counter electrode. All potentials were referred to an Ag/AgCl/KCl (3 mol L<sup>-1</sup>) electrode. Electrochemical measurements were performed at room temperature.

### 2.3 Preparation of SnO<sub>2</sub>@ multiwalled carbon nanotubes nanocomposite

The preparation of SnO<sub>2</sub>@MWCNTs was carried out according to [33] with modification. Briefly, about 20.5 mg of MWCNTs were placed into a beaker and dispersed in a mixture of 15 mL of ethanol and 15 mL of sulphuric acid and left for 24 hrs. The mixture was filtered under vacuum, followed by successive washing with deionized water and dried in an oven. The SnO<sub>2</sub>@MWCNTs

composites were prepared by a hydrothermal process; 15 mL ethyl alcohol, 15 mL distilled water, 20 mg purified MWCNTs, and 0.55 g cetyltrimethylammonium bromide (CTAB) were added to a 100 mL flask and the mixtures were sonicated using Branson 5800 ultrasonic system (UK) for 1 hour to disperse the MWCNTs uniformly. To the mixture, 0.08 g  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  was added and treated with mechanical agitation at 60 rpm for 45 min, then 4 mol  $\text{L}^{-1}$  sodium hydroxide (NaOH) solution was dropped to increase the pH to 12. Afterward, the mixed solution was transferred into an oven and kept at 100°C for 10h. Finally, the solid phase was filtered and washed with deionized water and ethanol respectively for several times, and dried in an oven at 70 °C.

#### 2.4 Sample collection and preparation

Surface water samples were from the East Rand region (Johannesburg South Africa) and were kept in 1000 mL polypropylene bottles. All water samples were acidified with nitric acid and stored in the fridge at 4°C until analysis. The elemental analysis was performed using the optimum conditions. Before analysis the samples were filtered through 0.2  $\mu\text{m}$  PVDF acrodisc syringe filter. The standard addition and calibration curve methods were used to determine the concentration of the target analytes in the samples.

#### 2.5 Modification of glassy carbon electrode

The modification of glass carbon electrode (GCE) was achieved using a simple casting method. Prior to modification, the GCE was polished with 1.0, 0.3 and 0.05  $\mu\text{m}$  alumina powder, respectively, and rinsed with doubly distilled water, followed by sonication in ethanol and doubly distilled water for 5 min, respectively, the GCE was allowed to dry. About 5 mg of  $\text{SnO}_2$ @MWCNTs was dispersed in 15 mL of DMF in a glass bottle for 30 minutes using ultrasonic homogenizer to obtain a homogeneous suspension.  $\text{SnO}_2$ @MWCNT electrode was prepared by casting 5  $\mu\text{L}$  MWCNT suspensions on the GCE surface using a micropipette. In order to allow evaporation of the solvent, the modified GCE was left to dry in a laminar flow at room temperature for about 24 h. Modified GCE was characterized by cyclic voltammetry and electrochemical impedance spectroscopy in a solution of 0.01 mol  $\text{L}^{-1}$   $\text{K}_3\text{Fe}(\text{CN})_6$ .

#### 2.6 Analytical procedure

Square wave anodic stripping voltammetric (SWASV) measurements were carried out in a 10 mL self-made electrochemical cell containing acetate buffer (pH 4.5) as supporting electrolyte medium. The  $\text{Tl}^+$  and  $\text{Hg}^{2+}$  ions were deposited at the potential of -1.2 to -0.8 V for 120s by the reduction of  $\text{Tl}^+$  and  $\text{Hg}^{2+}$ . The anodic stripping of the electrodeposited metals was performed in the potential range of -1.5 to 0.8 V. Before each measurement, pre-conditioning step was performed at the potential of 0.9 V vs. Ag/AgCl for 45 s. This was done in order to ensure disbanding of the remaining

deposits on the surface of the modified electrode. The peak currents at potentials about -0.76 and 0.18 V for  $\text{Tl}^+$  and  $\text{Hg}^{2+}$  were measured.

### 2.7 Optimization strategy of square wave anodic stripping voltammetric analysis

The effect of the most influential experimental parameters for the determination of trace elements using SWASV was investigated using experimental designs. In the first step which involves screening step, a two-level full factorial design was used. In the latter, three variables, that is, deposition time (DT), deposition potential (DP) and sample pH, were investigated (Table 1). Secondly, the central composite design was used to obtain the optimum conditions of the most influential factors such as deposition time (DT), deposition potential (DP) and sample pH. STATISTICA version 13 (Statsoft) software was used for processing experimental data.

**Table 1.** Levels of variables investigated for the optimization of SWASV conditions

Variables	Low level (-)	Center point (0)	High level (+)
pH	4	6.5	9
Deposition time (DT) (min)	60	180	300
Deposition potential (DP) (V versus SCE)	-1.2	-0.2	0.8

### 2.8 Comparative method

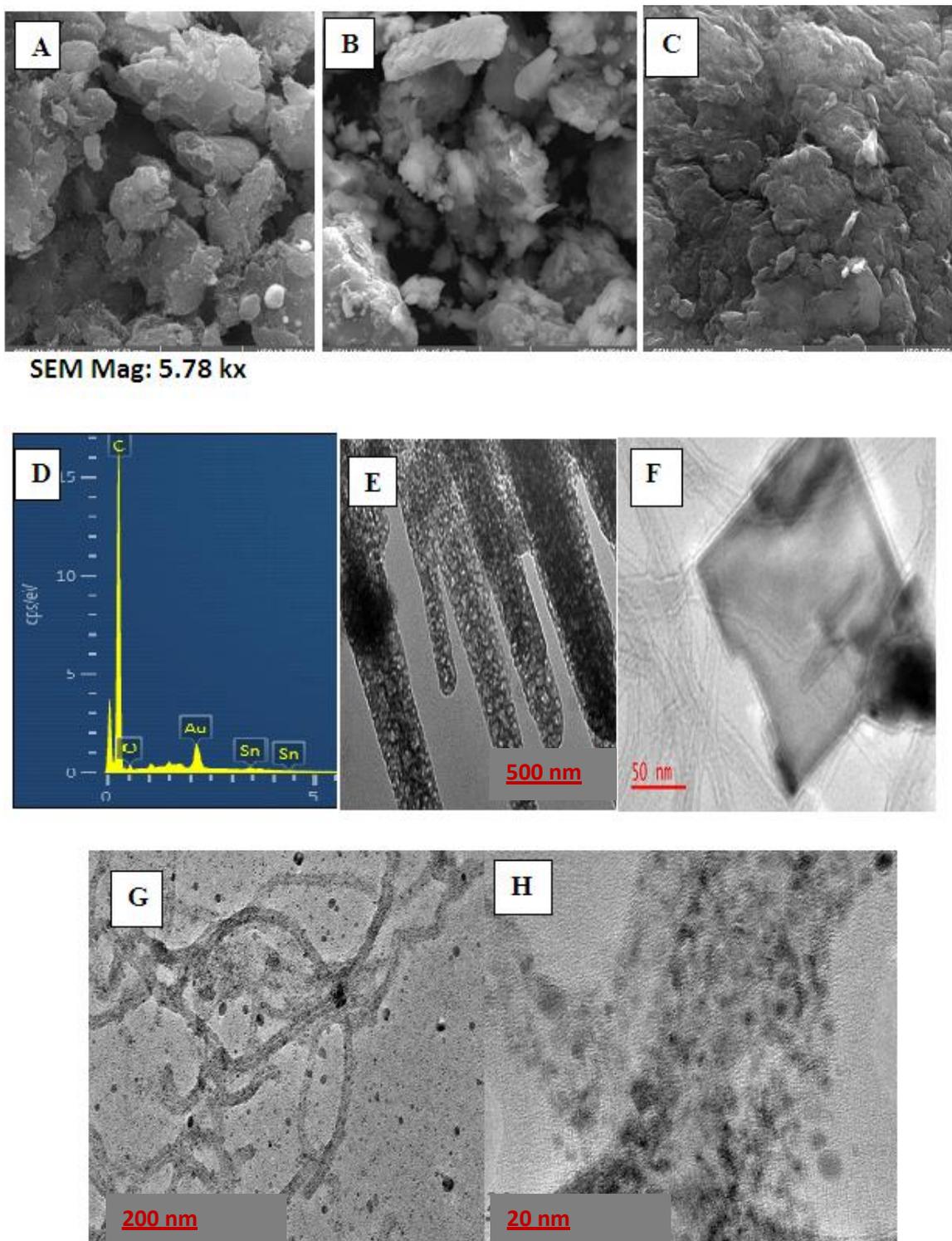
An inductively coupled plasma mass spectrometry (ICP-MS) was used as the reference method. ICP-MS experiments were performed on an Agilent 7900 (Agilent Technologies Inc., Tokyo, Japan) equipped with Ultra High Matrix Introduction (UHMI) option, octopole reaction system and an ASX-520 autosampler. Argon was used as plasma, make up and carrier gas while helium was used as collision gas in the octopole reaction system. Before all analyses, the ICP-MS was tuned using a 1.0 mg L<sup>-1</sup> solution of lithium (<sup>7</sup>Li), yttrium (<sup>89</sup>Y), thallium (<sup>205</sup>Tl) and cerium (<sup>140</sup>Ce). The ICP-MS drift was corrected by using bismuth as internal standard at a concentration of 1.0 mg L<sup>-1</sup>. Quality assurance and quality control (QC) of analysis included the analysis of blanks and quality control standard. In addition, after every 10 samples, QC standard and blanks were analysed.

## 3. RESULTS AND DISCUSSION

### 3.1. Characterization of SnO<sub>2</sub>@MWCNTs nanocomposites

The morphologies and structures of SnO<sub>2</sub>-MWCNTs were characterized by TEM and SEM/EDS (Fig. 1). The SEM image of SnO<sub>2</sub>/MWCNTs showed a more uniform surface (Fig. 1c). In addition, the EDS spectrum (Fig. 1d) confirmed the incorporation SnO<sub>2</sub>. The TEM for revealed that the

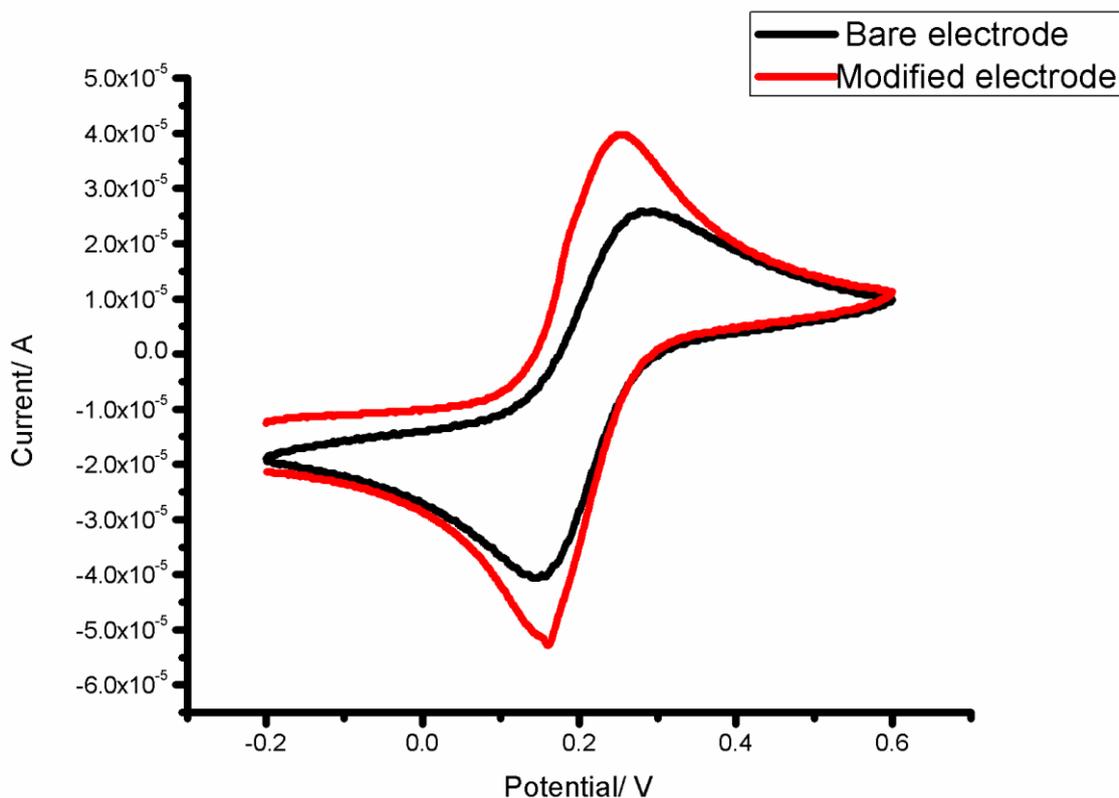
SnO<sub>2</sub> was homogeneously dispersed on the surface of MWCNTs (Fig. 1g-h). This suggests that the MWCNTs could be served as template for SnO<sub>2</sub> growth.



**Figure 1.** SEM for A) MWCNTs, B) SnO<sub>2</sub>, C) SnO<sub>2</sub>@MWCNTs nanocomposite and D) EDS for SnO<sub>2</sub>@MWCNTs; TEM images for E) MWCNTs, F) SnO<sub>2</sub>, G-H) SnO<sub>2</sub>@MWCNTs

### 3.3 Electrochemical characterization

Cyclic voltammetry is known to provide interface information of the electrode surface in dependence of the modification process. Therefore, to characterize the conductivity of modified and unmodified GCE, the cyclic voltammetric behaviour were carried using  $\text{Fe}_3(\text{CN})_6$  in 0.1 M KCl at potential scan rate of  $100 \text{ mV s}^{-1}$  (Fig. 2). It can be seen from this that a well defined CV redox process from  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  was observed at the bare GCE (Fig. 2a). In addition, it was observed that after the GCE was modified with  $\text{SnO}_2@\text{MWCNTs}$ , the redox couple peak currents increased. These results suggest that the introduction of  $\text{SnO}_2@\text{MWCNTs}$  can improve the electroactivity of the GCE electrode. These results further confirmed that the immobilization of  $\text{SnO}_2@\text{MWCNTs}$  onto GCE significantly enhanced the electrodes electroactivity, thus providing a suitable platform for detection of trace Hg and Tl. The significant increase of the estimated electroactive surface area was attributed to the combined unique properties of such as electrical conductivity and chemical sensitivity high surface area, chemical stability and high electrical conductivity [34].

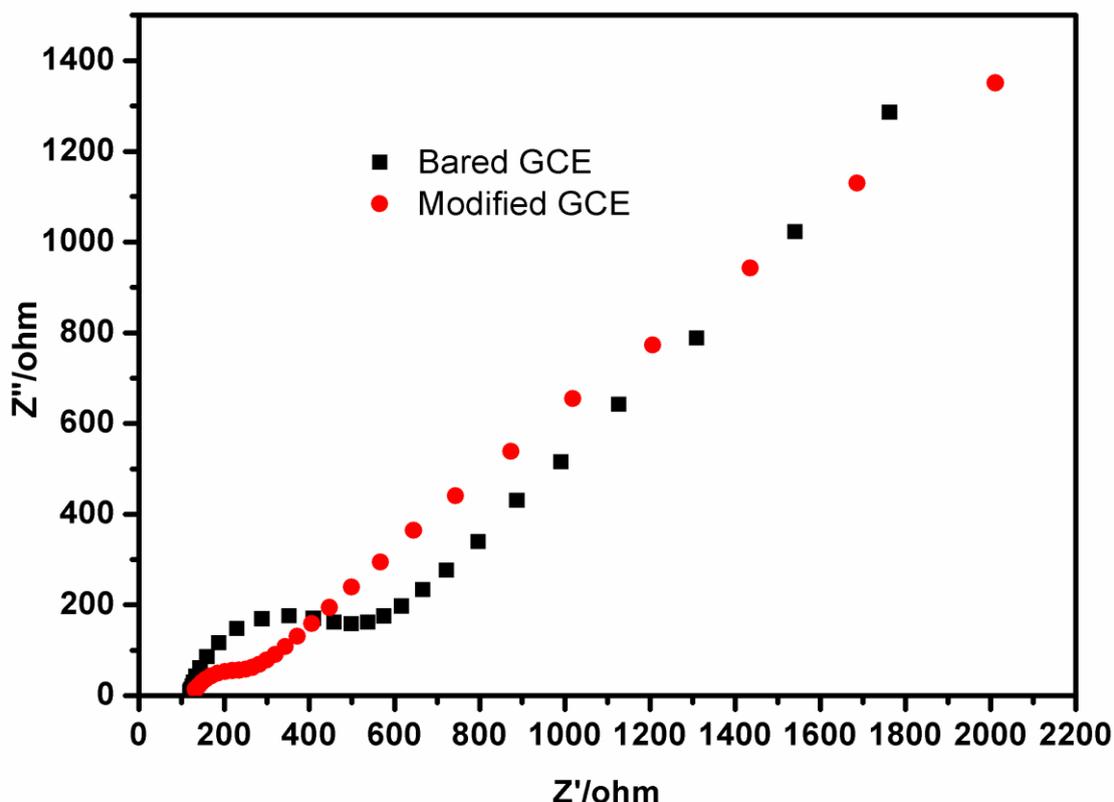


**Figure 2.** Cyclic voltammograms measured with bare and  $\text{SnO}_2@\text{MWCNTs}$  nanocomposite modified GCE in the solution of 5 mM  $\text{Fe}_3(\text{CN})_6$  containing  $0.1 \text{ mol L}^{-1}$  KCl.

### 3.4 Electrochemical impedance characterization of the GCE/ $\text{SnO}_2@\text{MWCNTs}$

Electrochemical impedance spectroscopy (EIS) is a technique that is used to investigate the surface dependent charge transfer process (interfacial properties such as resistance and capacitance) of

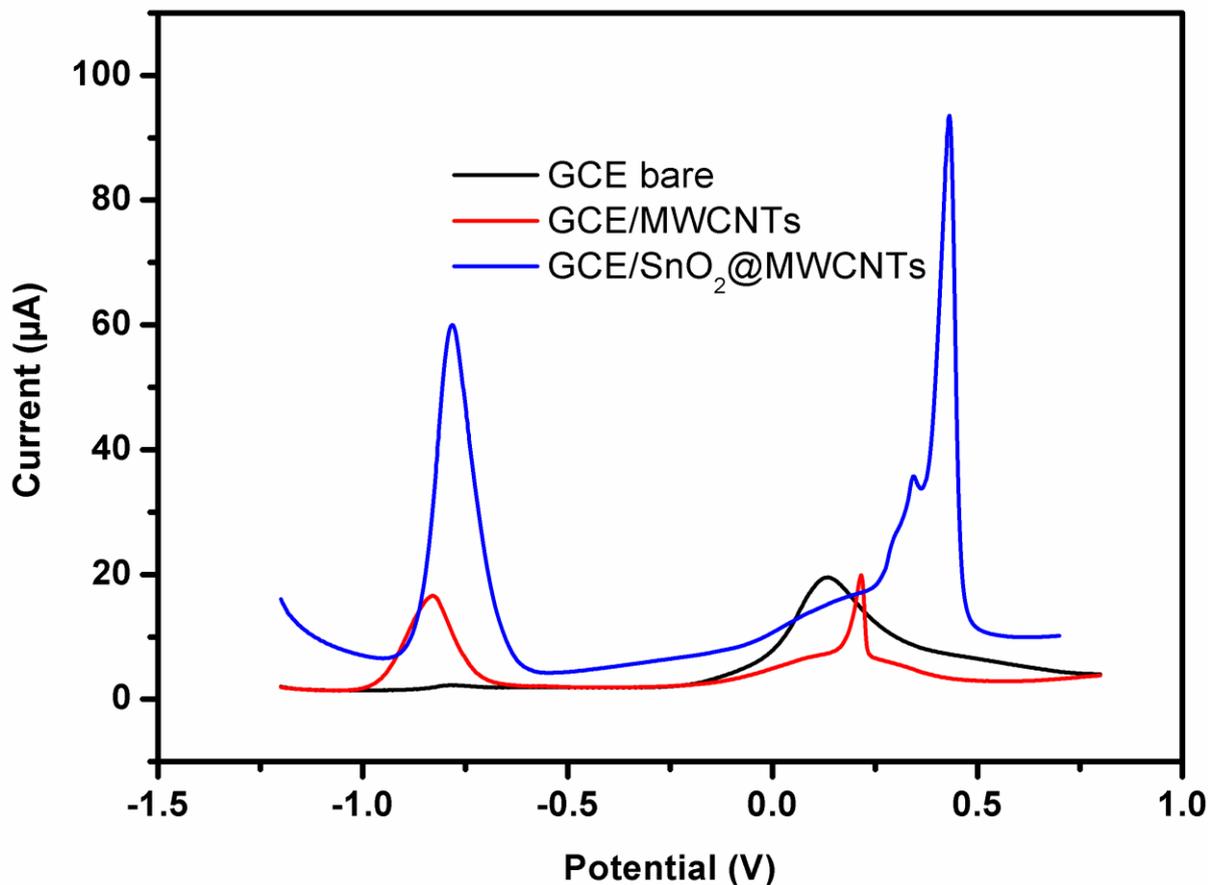
the electrode [34] Therefore, in this study, EIS was used to characterize the interface properties of the GCE/SnO<sub>2</sub>@MWCNTs. Fig. 3 presents the Nyquist plot of the electrochemical impedance spectra for the bare and SnO<sub>2</sub>/MWCNTs nanocomposite modified GCE. Typically, the Nyquist plot has a semicircle portion that corresponds to the electron-transfer resistance ( $R_{et}$ ) at a higher frequency range and a linear part at a lower frequency range that represents the diffusion-limited process [14]. It can be seen that compared to the base electrode, the modified GCE resulted in a decreased  $R_{et}$  value and it displayed an almost straight line. This observation was attributed to the promotion of the electron transfer process at the modified GCE surface [14]. These results were in agreement with the findings obtained from the cyclic voltammogram.



**Figure 3.** Nyquist diagram of electrochemical impedance spectra for bare GCE, SnO<sub>2</sub>, MWCNTs and modified GCE/SnO<sub>2</sub>@MWCNTs in the solution of 5 mM Fe<sub>3</sub>(CN)<sub>6</sub> containing 0.1 mol L<sup>-1</sup> KCl.

The simultaneous electrochemical detection of some trace elements such as Tl<sup>+</sup> and Hg<sup>2+</sup> is challenging on most electrodes because of the closeness of their peaks, resulting in an overlapped voltammetric response [36]. For this reason, to simplify the function of components in the electrode modification [36], the square wave stripping voltammograms of Tl<sup>+</sup> and Hg<sup>2+</sup> were recorded with various electrodes and are shown in Fig. 4. In the presence of trace metal ions using SnO<sub>2</sub>@MWCNTs, distinct oxidation peaks attributed to Tl<sup>+</sup> and Hg<sup>2+</sup> appeared at -0.76 and 0.18 V vs. Ag/AgCl, respectively. The voltammetric response for the unmodified electrode showed only one peak. This implied that the response obtained at the modified electrodes was enhanced due to the presence of SnO<sub>2</sub>@MWCNTs onto the electrode surface, the resulting separation in two peak potentials is sufficient to

achieve the accurate simultaneous determination  $Tl^+$  and  $Hg^{2+}$  in mixture samples in comparison with other studies [36]. On the other hand, the electrode response can be optimized for enhancing sensitivity, through surface modification[36].



**Figure 4.** Simultaneous detection of GCE, GCE/MWCNTs and GCE/SnO<sub>2</sub>@MWCNTs

### 3.6 Optimization of experimental SWASV parameters

The screening of the factors that could influence the simultaneous determination of Hg and Tl using SWASV in environmental samples was carried using a two-level full factorial design. The latter had three variables, that is, deposition time (DT), deposition potential (DP), and sample pH. The design matrix and analytical response (peak current) are presented in Supplementary Table S1. Analysis of variance (ANOVA) and p-values were used in order to evaluate the most influential factors to the analytical response. The Pareto charts (Fig. 5) reproduced from ANOVA results were used to visualize the main effects and their interactions [15]. According to the results in Fig. 1, for both Hg and sample pH, deposition time and all interactions showed poor influence on the analytical response while deposition potential was found to be significant at 95% confidence level. Since the objective of the study was the simultaneous determination of Hg and Tl, as well as taking into consideration the

importance of factors pH, DP, and DT for TI, response surface methodology based on central composite design (CCD) was used for further optimization.

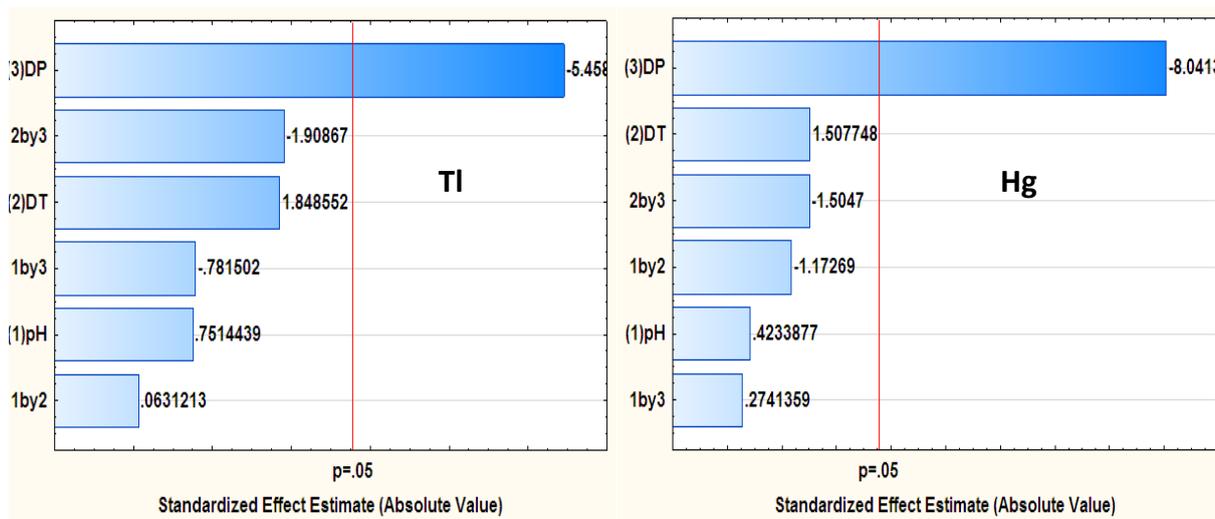


Figure 5. Pareto chart of standardized effects for variables in the determination of TI and Hg

Central composite design was used to evaluate and optimize main, interaction and quadratic effects of the most influential factors (pH, DP, and DT). The design matrix together with respective analytical responses for twenty experiments is presented in Table S2.

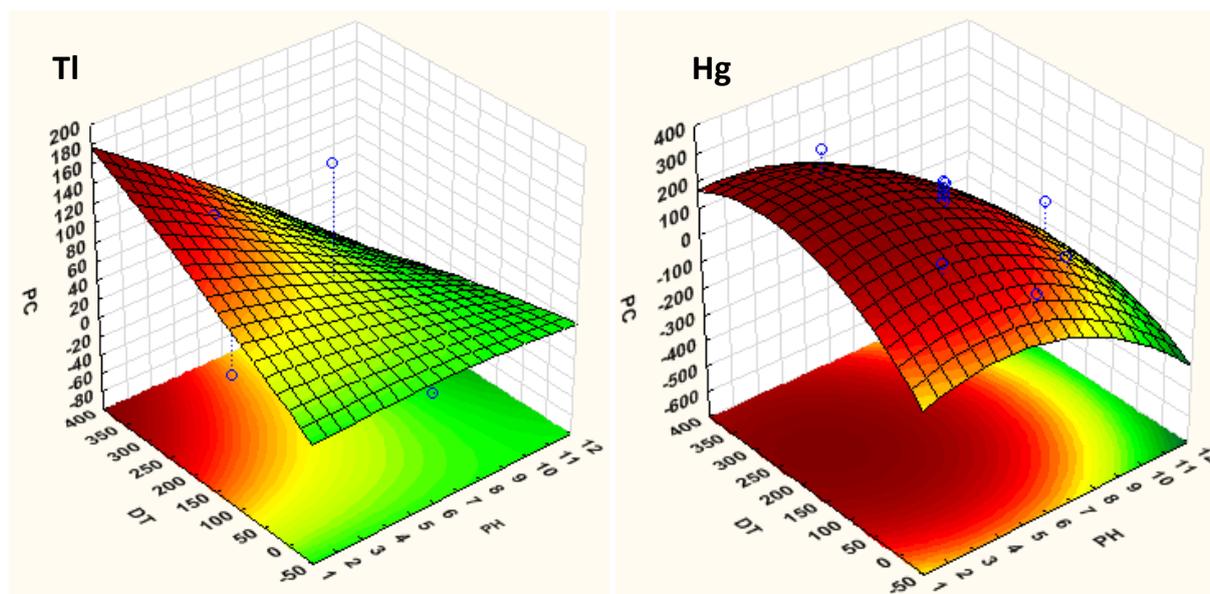


Figure 6. Response surface plots obtained for TI and Hg after electrochemical determination

The analysis of variance (ANOVA) produced from the data in Table S1 was used to evaluate the significance of the model equation and related terms [15]. In addition, the results for CCD were used to generate the response surfaces (Fig. 6). The latter was demonstrated by a quadratic equation

(for simplicity, equations are not included). According to the response surfaces and the quadratic, the overall optimum conditions that led to relatively high analytical responses for both analytes were found to be 4.5, -1.2 V and 180 min, for sample pH, deposition potential, and time, respectively.

### 3.6 Analytical performances

Under optimum conditions, the calibration curves were constructed using ten successive standard solutions at a concentration ranged from 0-500  $\mu\text{g L}^{-1}$ . Each calibration point was measure use six times using the same modified electrode. The useful linear dynamic ranges, correlation coefficients and calibration linear equations are shown in Table 2. The repeatability of the peak current expressed in terms of relative standard deviation (%RSD) at each calibration point ranged from 1.6-4.5%. The limit of detection (LOD) and quantification (LOQ) defined as  $LOD = \frac{3S_b}{m}$  and  $LOQ = \frac{10S_b}{m}$ , where,  $S_b$  and  $m$  are the standard deviation of the blank (n=15) and the slope (n = 6) of the calibration graph, respectively, are summarized in Table 2. The inter-day (repeatability) precision of the  $\text{SnO}_2\text{@MWCNTs-GCE}$  in the determination of  $\text{Hg}^+$  and  $\text{Hg}^{2+}$  was evaluated by performing ten determinations of the same standard solution containing 50  $\mu\text{g L}^{-1}$  of the target analytes. In addition, the intra-day (reproducibility) precision of the response was studied using seven electrodes prepared from the same batch in different days. The performance of these modified electrodes was evaluated by conducting the determination of 50  $\mu\text{g L}^{-1}$  of the target analyte model sample solution. The repeatability and reproducibility results (in terms of %RSD) of the  $\text{SnO}_2\text{@MWCNTs-GCE}$  ranged from 2.1-3.5 and 3.0-4.3%, respectively. These results revealed the suitability of simultaneous determination of  $\text{Tl}^+$  and  $\text{Hg}^{2+}$ . Under optimized conditions, the stability of modified electrode was investigated a period of three weeks by successive SWASV detection of mercury (II) and thallium (I). After two weeks and three day, the average %RSD for the peak current signal was 3.1 % and the peak potentials remain unchanged.

**Table 2.** Analytical figures of merit

Analytical parameters	$\text{Hg}^{2+}$	$\text{Tl}^+$
Dynamic linear range ( $\mu\text{g L}^{-1}$ )	0.004-400	0.003-450
Calibration linear equations	$I_{pa} (\mu\text{A}) = 0.0981C(\mu\text{g L}^{-1}) + 2.158$	$I_{pa} (\mu\text{A}) = 0.0889C(\mu\text{g L}^{-1}) + 3.158$
Correlation coefficients ( $r^2$ )	0.9987	0.9991
LOD ( $\text{ng L}^{-1}$ )	1.2	0.9
LOQ ( $\text{ng L}^{-1}$ )	4.0	3.0
Repeatability (%RSD)	3.5	2.1
Reproducibility (%RSD)	3.0	4.3
Stability (%RSD)	3.1	3.0

### 3.8 Comparison of the performance of GCE/SnO<sub>2</sub>@MWCNTs with other reported modified electrodes

A comparison of the developed GCE/SnO<sub>2</sub>@MWCNTs with other modified electrodes reported by other researchers for determination of Tl and Hg in environmental samples is summarized in Table 3. The LOD and LOQ obtained in this study were lower or similar to those reported by other authors in the literature. In addition, analytical performances of the current method revealed that the proposed SnO<sub>2</sub>@MWCNTs–GCE method has relatively high RSDs compared to in the literature listed in Table 3.

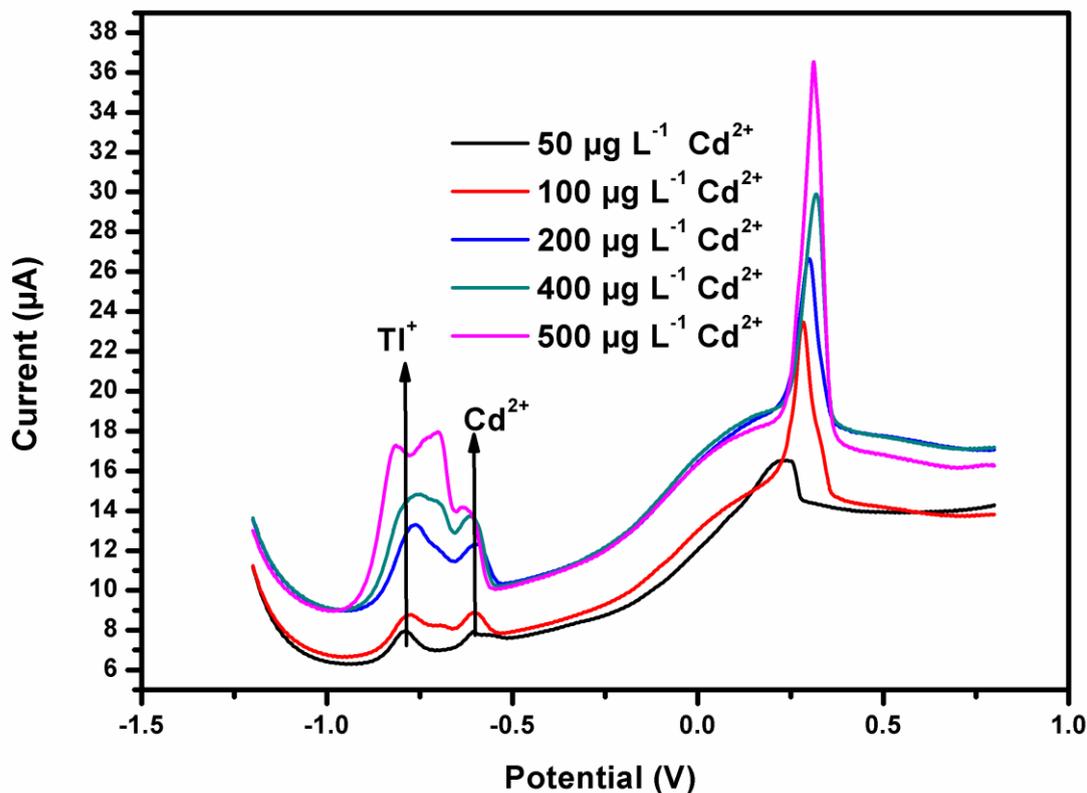
**Table 3.** Comparison of analytical performances of different modified electrodes for the determination of Tl<sup>+</sup> and Hg<sup>2+</sup> environmental samples

Method(electrode)	Analyte	LOD ( $\mu\text{g L}^{-1}$ )	Linear range ( $\mu\text{g L}^{-1}$ )	RSD%	Ref
Liquid/graphene GCE/ SWASV	Hg, Tl	0.09, 0.08	0.3-41	2.6-3.6	[36]
Au-SPCE/ SWASV	Hg	1.02	1-100	3.8	[37]
MCPE /DPV	Hg	0.2	0.5–150	3.4	[38]
BiABE/ DP ASV	Tl	0.001	0.1-1000	4.3	[39]
NG/GCE DPSV	Hg	1.03	200-1800	2.1 %	[40]
L-MSNPs/CPE/ SWASV	Hg	0.05	0.5–1000.0	4.7	[41]
BiFE/ASV	Tl	0.9-1.6	0.9–1.1	6.0–7.2	[42]
GO/SWASV	Tl	0.01	5-350	3.8	[43]
BFE/ SWASV	Tl	20	2.5-30.7	0.2	[44]
GCE/SnO <sub>2</sub> @MWCNTs	Hg, Tl	0.0012, 0.0009	0.003-450	2.1-4.0	This work

SWAV= square wave anodic stripping voltammetry/ GCE = glassy carbon electrode; Au-SPCE = gold screen printed carbon electrode; MCPE = magnetic carbon paste electrode, DPV = differential pulse voltammetry; DPSV = differential pulse stripping voltammetry; NG = N-doped graphene; ASV = anodic stripping voltammetry; L-MSNPs = silica nanoparticles, modified by a newly synthesized Schiff base ligand; CPE = carbon paste electrode; BiFe or BFE = bismuth film electrode

### 3.9 Interference study for Hg (II) and Tl (I) determination

Cadmium is generally considered as the major interference in the determination of thallium on mercury and carbon electrodes by ASV since the corresponding oxidation potentials are in close proximity to one another [36, 44]. SWASV were recorded after consecutive additions of Cd<sup>2+</sup> in a model sample solution containing fixed concentrations of Tl<sup>+</sup> and Hg<sup>2+</sup> (Fig. 7). As seen, no interference has been found in Tl<sup>+</sup> determination up to 400  $\mu\text{g L}^{-1}$  Cd<sup>2+</sup>. However, at 500  $\mu\text{g L}^{-1}$  Cd<sup>2+</sup>, their peaks partially overlap. Since the concentration of Cd in surface water is much lower than 500  $\mu\text{g L}^{-1}$ , accurate determination of Tl<sup>+</sup> can be achieved using the developed electrode. In addition, in cases where high concentration of Cd are expected, a suitable complexing/ chelating agent such EDTA can be used.



**Figure 7.** Interferences studies

In view of the above discussion, Cd is not only element that exists in environmental matrices. Therefore, the effect of multielement for the determination of  $\text{Hg}^{2+}$  and  $\text{Tl}^+$  was investigated. The analytical performance of  $\text{SnO}_2/\text{MWCNTs}$  in the presence of  $200 \mu\text{g L}^{-1}$  multielement solution mimicking the real water matrix revealed that  $\text{Tl}^+$  and  $\text{Hg}^{2+}$  can be accurately quantified.

### 3.10 Sample analysis

The applicability and validity of the proposed  $\text{SnO}_2/\text{MWCNTs}$ -GCE was investigated by its application to the determination of  $\text{Hg}^{2+}$  and  $\text{Tl}^+$  ions in 13 surface water samples. Generally, three millilitres of the water sample was pipette into a 10 mL calibrated flask containing 0.10 M acetate buffer solution (pH 4.5) and the developed method. Firstly, the accuracy of the developed method was assessed by analysing two water samples spiked with 2.00, 5.00 and 10.0  $\mu\text{g L}^{-1}$  Hg and Tl. The concentration of the target elements was achieved by comparing the values obtained by using both the standard addition curve method and calibration curve method. The results and percentage recovery values are shown in Table 4. According the results obtained a good agreement between the added and an obtained analyte concentration was obtained. The percentage recoveries ranged from 96.7-99.1%. These results revealed that that the developed electrochemical sensor method has relatively good accuracy in real sample matrix.

**Table 4.** Validation of the developed electrochemical sensor

Samples	Tl(I)			Hg(II)	
	Added ( $\mu\text{g L}^{-1}$ )	Found ( $\mu\text{g L}^{-1}$ )	Recovery (%)	Found ( $\mu\text{g L}^{-1}$ )	Recovery
SW1	0.00	0.831 $\pm$ 0.001	-	2.64 $\pm$ 0.02	-
	2.00	2.75 $\pm$ 0.05	96.0	4.63 $\pm$ 0.11	99.1
	5.00	5.80 $\pm$ 0.04	99.4	7.59 $\pm$ 0.02	99.0
	10.0	10.8 $\pm$ 0.07	99.6	12.6 $\pm$ 0.05	99.3
SW2	0.00	<LOD	-	2.29 $\pm$ 0.04	-
	2.00	1.96 $\pm$ 0.05	98.0	4.24 $\pm$ 0.05	97.5
	5.00	4.98 $\pm$ 0.03	99.6	7.25 $\pm$ 0.06	99.2
	10.0	9.97 $\pm$ 0.08	99.7	12.2 $\pm$ 0.09	99.5

In view of the above discussion, the developed method was further used for determination of the target analysis in the remaining ten surface water samples (Table 5). In addition, in order to investigate accuracy of the developed electrochemical sensor, we compared the results obtained by the proposed method against reference method (ICP-MS). At 95% confidence level, the results obtained by SnO<sub>2</sub>@MWCNTs–GCE sensor showed a good agreement with those obtained by ICP-MS (Table 5). This findings confirmed applicability and validity of the SnO<sub>2</sub>@MWCNTs–GCE sensor for precise and accurate determination of the mercury and thallium ions in environmental samples.

**Table 5.** Analysis of Tl(I) and Hg(II) in real water samples

Samples	Tl(I)		Hg(II)	
	SnO <sub>2</sub> @MWCNTs–GCE	ICP-MS	SnO <sub>2</sub> @MWCNTs–GCE	ICP-MS
SW 3	0.581 $\pm$ 0.02	0.592 $\pm$ 0.07	1.91 $\pm$ 0.10	1.92 $\pm$ 0.03
SW 4	0.224 $\pm$ 0.04	0.231 $\pm$ 0.06	2.14 $\pm$ 0.05	2.28 $\pm$ 0.06
SW 6	0.375 $\pm$ 0.03	0.381 $\pm$ 0.05	2.26 $\pm$ 0.03	2.35 $\pm$ 0.12
SW 7	<LOD	<LOD	1.71 $\pm$ 0.01	1.80 $\pm$ 0.04
SW 8	0.512 $\pm$ 0.01	0.515 $\pm$ 0.03	1.65 $\pm$ 0.11	1.75 $\pm$ 0.12
SW 9	0.437 $\pm$ 0.01	0.441 $\pm$ 0.01	1.99 $\pm$ 0.05	2.05 $\pm$ 0.08
SW 10	1.08 $\pm$ 0.05	1.11 $\pm$ 0.07	1.39 $\pm$ 0.09	1.45 $\pm$ 0.05
SW 11	<LOD	<LOD	1.38 $\pm$ 0.07	1.41 $\pm$ 0.02

<LOD = below limits of detection

#### 4. CONCLUSION

In this study, a glassy carbon electrode was modified with SnO<sub>2</sub>@MWCNTs for the electrochemical determination of trace Hg and Tl in surface water samples. The electrochemical determination was carried out using square wave anodic stripping voltammetry (SWASV). The influential factors affecting the experimental parameters for the determination of trace Hg and Tl were optimized using multivariate approach. The developed electrochemical sensor displayed wide linear

dynamic range, a relatively low detection limit, high precision and accuracy. In addition, the electrochemical characterization and analytical results revealed that the modified glassy carbon electrode had good electrochemical activity and high sensitivity for the determination of the target elements. The developed electroanalytical procedure was found to be suitable for the determination of ultra-trace levels of Hg(II) and Tl(I) in surface water samples and the results were not significantly different from those obtained by reference method.

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#### SUPPLEMENTARY DATA:

**Table S1.** Matrix of  $2^3$  full factorial designs (actual values) for the optimization of experimental parameters and the response values

EXPT	pH	DT	DP	PC ( $\mu\text{A}$ )	
				Tl	Hg
1	4	60	-1.2	34	81.1
2	9	60	-1.2	58	122
3	4	300	-1.2	95	169
4	9	300	-1.2	122	133
5	4	60	0.8	-12.5	-11.5
6	9	60	0.8	-13.6	0

<b>7</b>	4	300	0.8	-14.1	-11.4
<b>8</b>	9	300	0.8	-14	0
<b>9</b>	6.5	180	-0.2	0	68.9
<b>10</b>	6.5	180	-0.2	0	31.7
<b>11</b>	6.5	180	-0.2	0	33.3

**Table S2.** List of experiments in the Box-Behnken (actual values) for further optimization of SQWAV and the response values

<b>EXPT</b>	<b>pH</b>	<b>DT (min)</b>	<b>DP (V)</b>	<b>PC (<math>\mu</math>A)</b>	
				Tl	Hg
<b>1</b>	4	60	-1.2	35.3	76.1
<b>2</b>	9	60	-1.2	10.4	6.34
<b>3</b>	4	300	-1.2	107	110
<b>4</b>	9	300	-1.2	43.2	10.2
<b>5</b>	4	60	0.8	-1.83	-216
<b>6</b>	9	60	0.8	-2.52	-1.07
<b>7</b>	4	300	0.8	-2.39	-0.277
<b>8</b>	9	300	0.8	-1.33	0
<b>9</b>	2.3	180	-0.2	0	15.1
<b>10</b>	10.7	180	-0.2	0	0
<b>11</b>	6.5	0	-0.2	0	33.7
<b>12</b>	6.5	382	-0.2	0	0
<b>13</b>	6.5	180	-1.9	171	26.9
<b>14</b>	6.5	180	1.5	-3.82	0
<b>15</b>	6.5	180	-0.2	0	233
<b>16</b>	6.5	180	-0.2	0	208
<b>17</b>	6.5	180	-0.2	0	184
<b>18</b>	6.5	180	-0.2	0	162
<b>19</b>	6.5	180	-0.2	0	144
<b>20</b>	6.5	180	-0.2	0	126

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