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Voltammetric Analysis of Platinum Group Metals Using a Bismuth-Silver Bimetallic Nanoparticles Sensor

Charlton van der Horst, Bongiwe Silwana, Emmanuel Iwuoha and Vernon S. Somerset

Additional information is available at the end of the chapter

Abstract

This study dealt with the development of a bismuth-silver bimetallic nanosensor for differential pulse adsorptive stripping voltammetry of platinum group metals (PGMs) in environmental samples. The nanosensor was fabricated by drop coating a thin bismuth-silver bimetallic film onto the active area of the screen-printed carbon electrodes. Optimization parameters such as pH, dimethylglyoxime (DMG) concentration, deposition potential and deposition time, stability test and interferences were also studied. In 0.2 M acetate buffer (pH = 4.7) solution and DMG as the chelating agent, the reduction signal for PGMs ranged from 0.2 to 1.0 ng L^{-1}. In the study of possible interferences, the results have shown that Ni(II), Co(II), Fe(III), Na$^+$, SO$_4^{2-}$, and PO$_4^{3-}$ do not interfere with Pd(II), Pt(II), and Rh(III) in the presence of DMG with sodium acetate buffer as the supporting electrolyte solution. The limit of detection for Pd(II), Pt(II), and Rh(III) was found to be 0.07, 0.06 and 0.2 ng L^{-1}, respectively. Good precision for the sensor application was obtained with a reproducibility of 7.58% for Pd(II), 6.31% for Pt(II), and 5.37% for Rh(III) (n = 10).

Keywords: adsorptive stripping voltammetry, bismuth-silver bimetallic, platinum group metals, dimethylglyoxime, screen-printed electrode

1. Introduction

Nowadays, the pollution of surface waters with chemical contaminants is one of the most crucial environmental problems. These chemical contaminants enter rivers and streams resulting in tremendous amount of destruction to the aquatic ecosystem [1]. Heavy and platinum group metal (PGM) contaminations at trace levels in water resources present a major current environmental threat, so the detection and monitoring of these metal contaminants

result in an ever-increasing demand [2, 3]. According to El Mhammedi et al. [4], heavy metal analysis has been carried out in laboratories with time-consuming sampling, transportation and storage steps. Spectroscopy instrumentation was used for the simultaneous analysis of metal ions in water and, sediment biota samples. For the detection of trace metals, electrochemical analysis has always been recognized as a powerful tool [5–7].

In electroanalysis, much attention has been dedicated to the development of mercury-free sensors the last decade [8, 9]. Various materials have been used as working electrodes for heavy metal analysis [10, 11]. One of these working electrodes is bismuth film electrodes (BiFEs) and has been widely explored as a replacement for the toxic hanging drop mercury electrodes and films [12]. In differential pulse adsorptive stripping voltammetry (DPAdSV), nanoparticles play also a very important role. Due to their unique electronic, chemical, mechanical and thermal properties of nanoparticles make them extremely attractive for heavy metal electrochemical sensors in comparison with conventional materials [13]. In comparison with traditional macro-electrodes, nanoparticle electrodes show a decreased influence of the solution resistance, an increased mass-transport rate, and a higher signal-to-noise ratio [14].

Rahman et al. [15] use gold-silver bimetallic nanoparticles for the sensing of an environmental toxin, pyrene. These bimetallic nanoparticles were prepared by chemical reduction method involving the reduction of $AgNO_3$ and $HAuCl_4$ in aqueous solution of 2% hydrazine as reducing agent, cetryl trimethyl ammonium bromide as the capping agent, deionized water as the solvent and iso-octane as a co-precipitator. In another study, Mailu et al. [16] used overoxidized-polypyrrole/Ag-Au bimetallic nanoparticles for the determination of anthracene, using square wave voltammetry as technique. Bimetallic nanoparticles have been mainly used for the construction of biosensors and electrochemical sensors for determination of PGMs [17], arsenic [18], glucose and ascorbic acid [19], nitrite [20], carcinogenic organic compounds [21] and antidepressant drug [22].

This study focuses on the development of a new working electrode, such as bismuth-silver bimetallic nanoparticles for heavy metal analysis. The work done by Van der Horst et al. [23] describes the development of a DPAdSV procedure for the determination of platinum in environmental samples. In this procedure, a glassy carbon electrode modified with a bismuth film (GCE/Bi-AgF) was constructed. The optimization of several stripping voltammetric parameters such as dimethylglyoxime (DMG) concentration, composition of supporting electrolyte, pH, deposition potential and deposition time was performed. In this study, the results obtained showed low detection limits of 0.2 ng L^{-1} for Pt(II). These bismuth-silver bimetallic nanoparticles have been utilized for the determination of Pd(II), Pt(III), and Rh(III) [17] and Pt-Rh and Pd-Rh complexes [24] and the improved detection of ascorbic acid [25].

The main aim of the work described in this chapter was to investigate the construction and application of a disposable screen-printed carbon electrode (SPCE) that utilizes bismuth-silver bimetallic nanomaterials for PGMs determination. The electrochemical behavior of PGMs in road dust and roadside soil samples was investigated by voltammetry, and the optimum instrumental conditions were defined by DPAdSV measurements. The bismuth-silver

bimetallic screen-printed nanosensor was further successfully applied for the analysis of PGMs in environmental samples.

2. Materials and methods

2.1. Reagents

Sodium acetate (NaOAc), ammonia (NH$_3$) (25%), ammonium chloride (NH$_4$Cl), hydrochloric acid and nitric acid were supplied by Merck (South Africa). All precious and heavy metal standards (1000 mg L^{-1} AAS), dimethylglyoxime (DMG) were purchased from Sigma-Aldrich (South Africa). Glacial acetic acid (95%), ethanol (95%), hexamethylenetetramine (HMTA), dichloromethane, hydrazine sulfate, and formaldehyde solution were supplied by Kimix (South Africa). Poly(vinyl) alcohol (PVA) was also obtained from Sigma-Aldrich (South Africa). Next, 0.5–20 µg L^{-1} solutions of platinum group elements were prepared by diluting the corresponding standard stock solutions. A 0.01 M ammonia buffer solution (pH = 9.0) was prepared by mixing ammonium chloride with concentration ammonia and served as the supporting electrolyte. A 0.2 M sodium acetate buffer (pH = 4.7) was prepared by mixing sodium acetate with acetic acid and deionized water. The 0.01 M DMG solution was prepared in 95% ethanol and served as the chelating agent. All solutions were prepared by Milli-Q (Millipore 18 M Ohm cm) water.

2.2. Instrumentation

Differential pulse adsorptive stripping voltammetric measurements were performed using PalmSens® portable potentiostat/galvanostat, with the PS Trace program and accessories (PalmSens® Instruments BV, 3992 BZ Houten, The Netherlands). The portable potentiostat was connected to a microcomputer controlled by PS 2.1 software for data acquisition and experimental control. All the DPAdSV measurements were performed in a conventional electrochemical cell of 20.0 mL, employing the screen-printed carbon electrode modified with bismuth-silver nanoparticles (SCPE/Bi-Ag) with 4 mm diameter provided by Dropsens (Oviedo, Spain) as working electrodes [26–28]. All experiments were performed at ambient temperatures [29].

2.3. Preparation of the bismuth-silver bimetallic film

The Bi-Ag bimetallic nanoparticles were dispersed through ultrasonic vibration in a solution of *N,N*-dimethylformamide (DMF) to form a suspension. A defined quantity of the suspension was applied to a clean surface of SPCE and dried at room temperature to get a thin film on the SPCE surface [30–32]. After each voltammetric cycle, the cleaning of the Bi-Ag bimetallic nanofilm was performed by holding the potential of the electrode at +1.0 V. Traces of the remaining DMG complexes on the electrode surface were reduced and quickly desorbed at this potential. A short cleaning period of 30 s was required to refresh the electrode surface completely [33].

2.4. Procedure for the determination of PGMs

A 10 mL of 0.2 M acetate buffer (pH = 4.7) solution containing 1×10^{-5} M DMG was used as electrolyte in the cyclic and stripping voltammetric procedures. The SPCE/Bi-Ag nanosensor was immersed into the solution and an accumulation potential of −0.7 V (vs. Ag/AgCl) for Pd(II) and −0.6 V (vs. Ag/AgCl) for Pt(II), and −0.7 V (vs. Ag/AgCl) for Rh(III) was applied, while the solution was stirred. A 30 s quiet time was used, and the voltammogram was scanned from +0.8 to −1.4 V (vs. Ag/AgCl) at a scan rate of 60 mV s^{-1} for cyclic voltammetry measurements, while scanning was performed from −0.8 to −0.1 V (vs. Ag/AgCl) for adsorptive differential pulse stripping voltammetry measurements.

For dust or soil extracted solution, 1 mL aliquot of both extracted solutions was added to 9 mL of 0.2 M sodium acetate buffer (pH = 4.7) solution, containing 1×10^{-5} M DMG and 0.5 μg L^{-1} PGM standard, respectively, to give a final volume of 10 mL. The determination of Pd(II), Pt(II), and Rh(III) was performed using both adsorptive differential pulse stripping voltammetry (AdDPSV) [34]. The PGMs were introduced into the solution after the background voltammogram was recorded. All the experiments were performed in the presence of oxygen and at room temperature [35, 36].

3. Results and discussion

3.1. Electrochemical behaviors of Bi-Ag bimetallic modified electrode

The preliminary investigation of the electroactivity of the bismuth-silver bimetallic nanofilm electrode (Bi-AgFE) was done by using cyclic voltammetry (CV) and differential pulse adsorptive stripping voltammetry (DPAdSV) measurements. To obtain optimal conditions, it is very important to study the influence of supporting electrolyte, dimethylglyoxime concentration, deposition potential, deposition time, and stability test in DPAdSV mode. In this study, different electrolytes such as 0.1 M hydrochloric acid, 0.2 M sodium acetate (pH = 4.7), 0.1 M phosphate (pH = 7.0), and 0.1 M phosphate (pH = 9.0) buffers were tested as supporting electrolytes using the bismuth-silver bimetallic nanofilm electrode (Bi-AgFE). The cyclic voltammograms (CVs) of the resulting electrode obtained in the four different buffer solutions (not shown) showed that the redox response peak height was improved in the presence of 0.2 M sodium acetate buffer solution. Thus, for voltammetric measurements, a solution of acetic acid and sodium acetate was used as the optimal buffer solutions. The results obtained showed anodic peaks at −0.2 and −0.6 V (vs. Ag/AgCl) and cathodic peaks at +0.1 and +0.4 V (vs. Ag/AgCl). On closer inspection the CV results for Bi-AgFE sensor at a scan rate of 50 mV s^{-1}, it is seen that redox couples for Bi^{3+}/Bi^{2+}and Ag^{+}/Ag are present.

3.2. Effect of reagent concentration

In differential pulse adsorptive stripping voltammetric (DPAdSV) analysis, the ligand concentration in solution has a profound effect on the voltammetric peak height. Palladium has a definite adsorption voltammetric peak in acidic medium if dimethylglyoxime (DMG) is

used as complexing agent. Dimethylglyoxime is suggested by Georgieva and Pihlar [37] as the complexing agent if sodium acetate is used as supporting electrolyte. In this investigation, the effect of DMG concentrations on the PGMs (Pd, Pt, Rh) peak currents was examined in the range from 5×10^{-6} to 5×10^{-5} M (**Figure 1**). The effect of DMG concentration on Pd(II), Pt(II), and Rh(III) peak currents in 0.2 M sodium acetate buffer (pH = 4.7) solution has shown that concentration of 1×10^{-5} M DMG gave the best results for the SPCE/Bi-AgF sensor, and it was decided to conduct all other stripping experiments using this DMG concentration. **Figure 1** presents the results for the current responses of PGMs complexes ((e.g., Pd(HDMG)$_2$, Pt(HDMG)$_2$, Rh(HDMG)$_3$) and the evaluated potentials in different concentrations of DMG.

3.3. Deposition potential and time studies

In electroanalytical chemistry, differential pulse voltammetry (DPV) is used as an effective and common technique when the content of analyte is very low due to its sensitivity [38]. The influence of deposition potential (E_d) and time (t_d) is always important factors on the
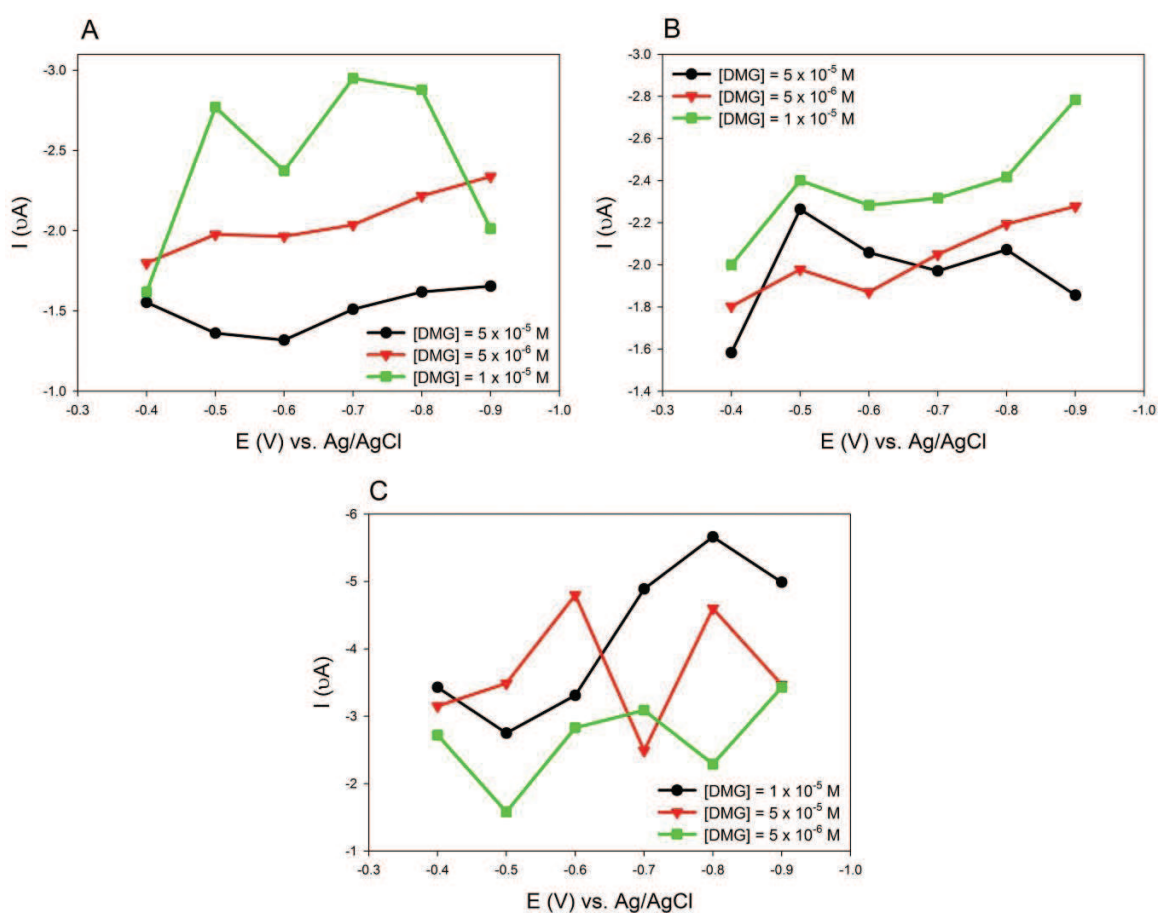

Figure 1. Effect of varying dimethylglyoxime (DMG) concentrations on the peak current results for PGMs at a SPCE/Bi-AgFE sensor. The solutions consisted of 0.2 M acetate buffer, (pH = 4.7) containing: (A) 1 ng L^{-1} Pd(II) with deposition time of 30 s V; (B) 1 ng L^{-1} Pt(II) with deposition time of 30 s; and (C) 1 ng L^{-1} Rh(III) with deposition time of 30 s. Three different concentrations of DMG were employed as demonstrated in the graphs.

sensitivity and detection limit in DPV methods. To enhance the electroanalytical performance of the Bi-Ag bimetallic sensor, the deposition potential and time were optimized. The dependence of deposition potential on the variation of stripping peak current for 1 ng L^{-1} Pd(II), Pt(II), and Rh(III) at the bismuth-silver nanosensor surface (**Figure 2A**). The optimization of deposition potential was done by varying the potential from −0.4 to +1.0 V (vs. Ag/AgCl). In the optimization results for deposition potentials have shown that for Pd(II) and Pt(II), a steady increase in the peak current responses was observed up to a E_d value of −0.7 and −0.9 V (vs. Ag/AgCl). In the case for Rh(III), a sharp increase in peak current was observed at −0.9 V (vs. Ag/AgCl). Optimum deposition potential for Pd(II), Pt(II) and Rh(III) determination in 0.2 M acetate buffer (pH = 4.7) solution is in the range from −0.7, −0.9 and −0.8 V (vs. Ag/AgCl), respectively.

The dependence of deposition time on the stripping peak current of Pd(II), Pt(II) and Rh(III) was investigated using the bismuth-silver bimetallic nanosensor (**Figure 2B**). In adsorptive stripping voltammetry (ASV), complexing agent in the electrolyte solution, after reaction, forms complex ions in the solution, and the complex is accumulated onto the sensor surface in the amount proportional to the deposition time [39]. The dependence of deposition time on the stripping peak current for Pd(II) and Rh(III) decreases almost linearly with longer deposition times. A deposition time at 30 s was chosen as the optimum deposition time in this investigation. In the case for Pt(II), stripping peak current increases with the increasing in the deposition time between 30 and 90 s and became nearly constant above 90 s due to the surface saturation of the bismuth-silver bimetallic nanosensor. In this study for all subsequent Pt(II) measurements, deposition time of 90 s was employed due to surface saturation of the bimetallic sensor.

Table 1 illustrates a summary of the optimized working conditions for the adsorptive differential pulse stripping voltammetric (AdDPSV) determination of a series of standard (or model) solutions of Pd(II), Pt(II), and Rh(III) metal ions. It was observed that Pd(II) and Rh(III) have the same deposition time with different deposition potentials. Other optimized working conditions such as DMG concentration, supporting electrolyte and potential window was the same for of Pd(II), Pt(II), and Rh(III) throughout the study.
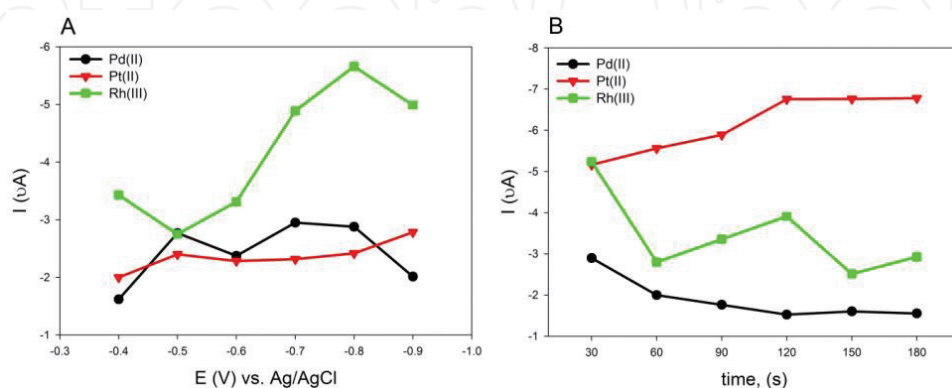
Figure 2. Results obtained for the effect of: (A) varying deposition potential (E_d) upon adsorptive stripping voltammetric responses for 1 ng L^{-1} Pd(II), Pt(II) and Rh(III); and (B) varying deposition times (t_d) upon adsorptive stripping voltammetric responses for 1 ng L^{-1} Pd(II), Pt(II) and Rh(III) at the SPCE/Bi-AgFE sensor. The solutions used consisted of 0.2 M acetate buffer (pH = 4.7) containing 1×10^{-5} M DMG concentration.

Stripping step	Determinant	Pd(HDMG)$_2$	Pt(HDMG)$_2$	Rh(HDMG)$_3$
	pH	4.7		
	Reduction potential (V)	−0.7	−0.9	−0.8
	Deposition time (s)	30	90	30
	Supporting electrolyte	0.2 M NaOAc		
Measurement	Measurement technique	DPSV		
	Potential window	0.1 to −0.6 V		
	Supporting electrolyte	0.2 M NaOAc		
	DMG concentrations (M)	Current (μA)		
	5 × 10^{-6}	−2.038	−2.278	−4.600
	1 × 10^{-5}	−2.950	−2.784	−5.660
	5 × 10^{-5}	−1.511	−1.856	−2.290

Table 1. Summary of optimum stripping voltammetry conditions for the determination of Pd(II), Pt(II) and Rh(III) with the constructed GC/Bi-AgFE bimetallic nanosensor [40].

3.4. Analytical features of the adsorptive stripping procedure

According to the literature, the determination of palladium by DPAdSV at the surface of the hanging mercury drop electrode (HMDE) was first described by Wang and Varughese [41]. Dimethylglyoxime was used as the complexing ligand in slightly acidic media (pH = 5.15) for the deposition of palladium-dimethylglyoxime complex (Pd-(HDMG)$_2$). In the present study, the determination of Pd-(HDMG)$_2$ was done in 0.2 M acetate buffer (pH = 4.7) solution at the surface of a bismuth-silver bimetallic nanosensor. The DPAdSV current of the Pd-(HDMG)$_2$ complex at optimal conditions yielded well-defined peaks, in the concentration range 0.4–1.0 ng L^{-1} shown in **Figure 3A**. The five concentrations used yielded a linear response and the equation of the linear calibration curve is $y = 0.773x + 0.6151$ with a correlation coefficient of 0.9911.

The differential pulse adsorptive stripping voltammetric (DPAdSV) current for the Pt-(HDMG)$_2$ complex was measured at optimal conditions using a bismuth-silver bimetallic nanosensor in **Figure 3B**. In these measurements, a series of Pt-(HDMG)$_2$ complex concentrations ranging from 0.2 to 0.8 ng L^{-1} in 0.2 M acetate buffer (pH = 4.7) solution with 30 s deposition time was used. The peaks observed in the differential pulse voltammograms are well defined and the five concentrations used yielded a linear response, and the equation of the linear calibration curve is $y = 0.690x + 0.718$ with a correlation coefficient of 0.9881.

The determination of the Rh-(HDMG)$_3$ complex in 0.2 M acetate buffer (pH = 4.7) solution was performed by DPAdSV analysis under optimized working conditions, and the voltammograms are shown in **Figure 3C**. Well-defined stripping peaks were observed at
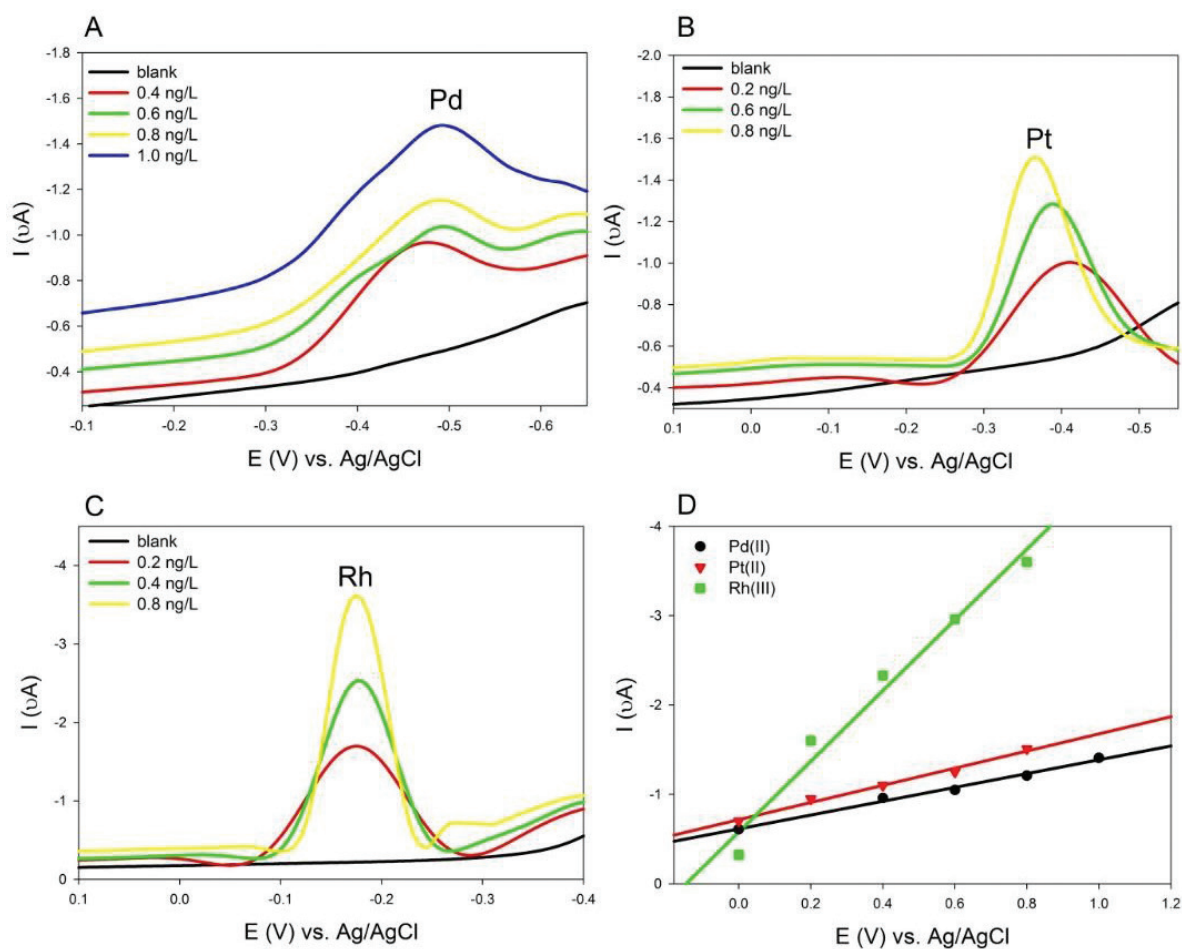
Figure 3. Differential pulse adsorptive stripping voltammetry results for increasing concentrations of (A) 0.4–1.0 ng L^{-1} Pd(II) with E_d = −0.7 V (vs. Ag/AgCl), (B) 0.2–0.8 ng L^{-1} Pt(II) with E_d = −0.9 V (vs. Ag/AgCl) and t_d = 120 s, (C) 0.2–0.8 ng L^{-1} Rh(III) with E_d = −0.7 V (vs. Ag/AgCl) and t_d 30 s at a SPCE/Bi-AgFE sensor, (D) corresponding calibration curves for the obtained DPAdSV curves. The electrolyte used consisted of 0.2 M acetate buffer (pH = 4.7) containing 1×10^{-5} M DMG concentration.

the bismuth-silver bimetallic nanosensor in the concentration ranging from 0.2 to 0.8 ng L^{-1}. The results indicated that dimethyglyoxime (DMG) can greatly promote the deposition of the Rh-(HDMG)$_3$ complex at the bismuth-silver bimetallic nanosensor and significantly increase the sensitivity of the determination of the Rh-(HDMG)$_3$ complex. The inset in **Figure 3C** showed that the DPAdSV peak currents have a linear response for the five concentrations evaluated, and the equation of the linear calibration curve is $y = 3.9527x + 0.5798$, with a correlation coefficient of 0.9703.

3.5. Interference and stability studies

In differential pulse adsorptive stripping voltammetry (DPAdSV), several trace metals can interfere with the determination of platinum group metals (PGMs) absorbing competitively onto the bismuth-silver bimetallic film electrode (Bi-AgFE) surface. They also complexing

competitively with DMG producing signals close to that of the different PGMs or completely suppress the peaks. A number of metal ions that could potentially interfere with these PGMs were investigated such as Ni(II), Co(II), Fe(III), and Na+. The sulfates and phosphates were also investigated, and 1 ng L^{-1} of these interfering ions was added to the model solutions. These ions were chosen because they might reasonably be expected to exhibit redox activity at the SPCE/Bi-AgF sensor and exist in real samples. The behavior of Pd(II), Pt(II), and Rh(III) at concentrations of 0.5–1.5 ng L^{-1} in the presence of these cations and anions was investigated. This study showed that these ions have not interferes on the determination of Pd(II), Pt(II) and Rh(III).

The stability of the fabricated bismuth-silver bimetallic nanosensor was investigated for the peak current after every 7 h over a period of 28 h. The electrode was kept in deionized water after each measurement. Using the above optimized conditions, the bismuth-silver bimetallic nanosensor was utilized for the determination of 1 ng L^{-1} concentration of the PGMs evaluated. It was found that the peak current intensities decreased only slightly for the bismuth-silver bimetallic nanosensor, indicating that the nanosensor has good stability and repeatability (data not shown).

3.6. Analysis of environmental samples

The determination of PGMs was conducted in road dust and roadside soil samples collected in the Western Cape Province at Bottelary Road close to Stellenbosch and Old Paarl Road close to Klapmuts, outside Stellenbosch using the SPC/Bi-AgFE nanosensor. The bioavailability of the PGMs in the road dust and roadside soil samples was determined by subjecting the samples to a three-step sequential extraction procedure [42, 43].

The two sets of results obtained for road dust and roadside soil samples are shown in **Table 2**. The results for the dust and soil samples have shown that the method was successfully applied using the SPC/Bi-AgFE nanosensor. Relatively good results were obtained for

	DPAdSV		
	Carbonate bound	Organic bound	Fe-Mn bound
Sample	Pd(II) (ng L^{-1})	Rh(III) (ng L^{-1})	Pt(II) (ng L^{-1})
BOT1[#]	4.33 ± 0.21	4.39 ± 0.28	1.68 ± 0.07
BOT2[#]	3.68 ± 0.15	2.16 ± 0.27	0.90 ± 0.01
BOT3[#]	3.85 ± 0.20	12.68 ± 0.31	1.28 ± 0.01
BOT4[#]	4.25 ± 0.38	1.87 ± 0.38	0.56 ± 0.53
OP1[#]	2.56 ± 0.04	0.71 ± 0.10	1.54 ± 0.14
OP2[#]	3.05 ± 0.31	1.58 ± 0.08	2.39 ± 0.05
OP3[#]	2.74 ± 0.06	0.78 ± 0.10	8.78 ± 0.61
OP4[#]	4.29 ± 0.07	1.82 ± 0.32	2.96 ± 0.97

	DPAdSV		
	Carbonate bound	Organic bound	Fe-Mn bound
BOT1[*]	4.87 ± 0.22	5.98 ± 0.26	1.84 ± 0.12
BOT2[*]	3.68 ± 0.23	3.02 ± 0.29	1.18 ± 0.28
BOT3[*]	3.55 ± 0.42	15.93 ± 0.76	2.35 ± 0.26
BOT4[*]	4.55 ± 0.24	7.10 ± 0.45	1.23 ± 0.04
OP1[*]	2.82 ± 0.08	1.12 ± 0.07	2.17 ± 0.03
OP2[*]	3.87 ± 0.20	1.49 ± 0.15	2.57 ± 0.13
OP3[*]	3.22 ± 0.37	1.40 ± 0.14	5.09 ± 0.55
OP4[*]	4.53 ± 0.14	4.09 ± 0.54	1.08 ± 0.44

BOT, Bottelary Road; OP, Old Paarl Road.
[#] Roadside dust.
[*] Roadside soil.

Table 2. Results obtained for the determination of PGMs concentrations using a SPC/Bi-AgFE nanosensor in dust and roadside soil samples collected from roads near Stellenbosch, Western Cape Province.

using the DPAdSV method. For high accuracy and sensitivity, only single PGM analysis was determined in all experiments using the constructed electrochemical sensor. These results indicate that the constructed SPC/Bi-AgFE nanosensor is more sensitive toward the determination of Pd(II), Pt(II) and Rh(III) in dust and soil samples.

3.7. Comparison of calculated results for different sensor platforms

To calculate the limit of detection (LOD), the formula 3σ/slope was employed, where σ is the standard deviation of the blank. The LODs of Pd(II), Pt(II), and Rh(III) obtained under the optimized conditions of these method were 0.7 ng L^{-1} for Pd(II), 0.06 ng L^{-1} for Pt(II), and 0.2 ng L^{-1} for Rh(III) for the SPC/Bi-AgFE nanosensor. In this study, the developed SPCE/Bi-AgFE nanosensor showed lower limit of detection than previously reported sensors based on the detection of PGMs in environmental samples. To illustrates the repeatability of the sensor, the relative standard deviation (RSD) was calculated and found to be 7.58% for Pd(II), 6.31% for Pt(II), and 5.37% for Rh(III) ($n = 10$). The reproducibility was evaluated using three different electrodes and a solution containing 1.0 ng L^{-1} of each metal ion with a RSD of 6.81% for Pd(II), 5.11% for Pt(II), and 5.97% for Rh(III).

The analytical performance of the SPC/Bi-AgFE nanosensor was compared with those obtained by other electrochemical sensors described in the literature for the determination of PGMs and illustrated in **Table 3** [35, 36, 44]. From the studies of modified electrodes, this SPC/Bi-AgFE nanosensor revealed lower limits of detection compared to the reported electrodes for PGMs determination. This developed procedure also reveals high sensitivity and faster response time for PGMs analysis in the presence of DMG, using acetate buffer (pH = 4.7) solution as the supporting electrolyte.

Electrode	Method	Linear range	LOD	References
SPC/Bi-AgFE	AdDPSV	Pd(II): 0.4–1.0 ng L^{-1} Pt(II): 0.2–0.8 ng L^{-1} Rh(III): 0.2–0.8 ng L^{-1}	Pd(II) – 0.07 ng L^{-1} Pt(II) – 0.06 ng L^{-1} Rh(III) – 0.2 ng L^{-1}	This work
GC/Bi-AgFE	AdDPSV	Pd(II): 0.2–1.0 ng L^{-1} Pt(II): 0.2–1.0 ng L^{-1} Rh(III): 0.4–1.0 ng L^{-1}	Pd(II) – 0.19 ng L^{-1} Pt(II) – 0.20 ng L^{-1} Rh(III) – 0.22 ng L^{-1}	[17]
SPC/BiFE	AdDPSV	Pd(II): 0–0.1 μg L^{-1} Pt(II): 0.2–0.1 μg L^{-1} Rh(III): 0–0.08 μg L^{-1}	Pd(II) – 0.008 μg L^{-1} Pt(II) – 0.006 μg L^{-1} Rh(III) – 0.005 μg L^{-1}	[35]
GC/BiFE	AdDPSV	Pd(II): 0–2.0 μg L^{-1} Pt(II): 0–3.5 μg L^{-1} Rh(III): 0–3.0 μg L^{-1}	Pd(II) – 0.19 μg L^{-1} Pt(II) – 0.20 μg L^{-1} Rh(III) – 0.22 μg L^{-1}	[36]
CGMDE	CAdSV	Pt(II): 2.0–80.0 μg L^{-1} Rh(III): 1.0–160.0 μg L$^-$	Pt(II) – 0.60 μg L^{-1} Rh(III) – 0.20 μg L	[44]
CGMDE	CAdSV	Pt(II): 5.0 × 10^{-12} to 1.5 × 10^{-9} mol L^{-1}	Pt(II) – 0.03 μg L^{-1}	[39]
Hg(Ag)FE	CSV	Pd(II): 1–50 μg L^{-1}	Pd(II) – 0.15 μg L^{-1}	[45]

Table 3. Comparison of results obtained in present work with other modified stripping voltammetric procedures for the determination of PGMs in model standard solutions and environmental samples are listed.

4. Conclusion

In conclusion, the construction, optimization, and practical application of the SPC/Bi-AgFE nanosensor, which were prepared by drop-coating onto a screen-printed carbon electrode, have been presented. The important DPAdSV parameters were optimized, and well-defined peaks were obtained for Pd(II), Pt(II) and Rh(III) in model standard solutions. To illustrate the practical application of the developed SPC/Bi-AgFE nanosensor, the sensor was tested for the detection of PGMs in road dust and roadside soil samples, collected from the Bottelary and Old Paarl Roads near Stellenbosch in the Western Cape Province. The results obtained for the developed nanosensor provide an alternative sensor platform to replace toxic mercury electrodes and can be used for routine determination of PGMs in road dust and roadside soil with high sensitivity.

Acknowledgements

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