Spectroscopic and Voltammetric Analysis of Platinum Group Metals in Road Dust and Roadside Soil

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Abstract: The emission of toxic compounds by increasing anthropogenic activities affects human health and the environment. Heavy road traffic and mining activities are the major anthropogenic activities contributing to the presence of metals in the environment. The release of palladium (Pd), platinum (Pt), and rhodium (Rh) into the environment increases the levels of contamination in soils, road sediments, airborne particles, and plants. These Pd, Pt, and Rh in road dusts can be soluble and enter aquatic environment posing a risk to environment and human health. The aim of this study is to determine the levels of Pd, Pt, and Rh with spectroscopy and voltammetric methods. Potential interferences by other metal ions (Na(I), Fe(III), Ni(II), Co(II)) in voltammetric methods have also been investigated in this study. At all the sampling sites very low concentrations of Pd, Pt, and Rh were found at levels that range from 0.48 ± 0.05 to 5.44 ± 0.11 ng/g (dry weight (d.wt)) for Pd(II), with 17.28 ± 3.12 to 81.44 ± 3.07 pg/g (d.wt) for Pt(II), and 14.34 ± 3.08 to 53.35 ± 4.07 pg/g (d.wt) for Rh(III). The instrumental limit of detection for Pd, Pt, and Rh for Inductively Coupled Plasma Quadrupole-based Mass Spectrometry (ICP-QMS) analysis was found to be 3×10^{-6} µg/g, 3×10^{-6} µg/g and 1×10^{-6} µg/g, respectively. In the case of voltammetric analysis the instrumental limit of detection for Pd(II), Pt(II), and Rh(III) for differential pulse adsorptive stripping voltammetry was found to be 7×10^{-8} µg/g, 6×10^{-8} µg/g, and 2×10^{-7} µg/g, respectively. For the sensor application, good precision was obtained due to consistently reproduced the measurements with a reproducibility of 6.31% for Pt(II), 7.58% for Pd(II), and 5.37% for Rh(III) ($n = 10$). The reproducibility for ICP-QMS analysis were 1.58% for Pd(II), 1.12% for Pt(II), and 1.37% for Rh(III) ($n = 5$). In the case of repeatability for differential pulse adsorptive stripping voltammetry (DPAdSV) and ICP-QMS, good standard deviations of 0.01 for Pd(II); 0.02 for Pt(II), 0.009 for Rh(III) and 0.011 for Pd, 0.019 for Pt and 0.013 for Rh, respectively.

Keywords: inductive coupled plasma spectroscopy; differential pulse adsorptive stripping voltammetry; dust; soil; platinum group metals; extraction methods

1. Introduction

Platinum (Pt), palladium (Pd), and rhodium (Rh) (also referred to as platinum group metals (PGMs)) are released into the environment by anthropogenic activities such as road traffic, hospitals, and mining industries [1]. The release of Pt, Pd, and Rh by road traffic has attracted much interest and attention in recent years. The most serious problems of road traffic are the emissions of toxic substances such as oxides of sulfur, carbon monoxide, nitrogen oxides, aldehydes (formaldehydes, acetaldehyde and benzaldehyde), hydrocarbons (alkanes, alkenes and alkynes), and heavy metals into the environment. In developed countries, the emission of air pollutants associated with road

traffic (e.g., carbon monoxide (CO), nitrogen oxides (NOx), and hydrocarbons (HCs)) have decreased significantly from 35% to 24% depending on the type of pollutant, which is due to the introduction of exhaust catalysts [2,3]. The disadvantage of using exhaust catalysts containing Pt, Pd, and Rh, is the release into the environment. Platinum, Pd, and Rh are mainly emitted as fine suspended particulate matter from vehicle exhaust emissions.

Nowadays, the determination of Pt, Pd, and Rh in environmental materials increased since use as exhaust catalysts [4]. An increase of Pt, Pd, and Rh concentrations has occurred in the catalyst dust along roadways, on adjacent vegetation and soil, and in water bodies either directly or through runoff [5]. In work done by Hooda et al. [6], the results for the determination of Pt, Pd, and Rh in soil samples nearby roads showed that the concentrations of these metals decreased with the increasing distance of the sampling spot from the road, while the highest concentrations were found in the range of two meters from the road.

In the metallic state Pt, Pd, and Rh are non-toxic and non-allergenic, but some of their compounds, especially the chlorinated ones, are very toxic and allergenic [7,8]. In literature, the indications of acute toxicity of several PGM-chlorinated salts has been identified and evidence of (deoxyribonucleic acid) DNA damage due to Pt, Pd, and Rh exposure has been observed for both in vitro and in vivo [7–9]. Platinum, Pd, and Rh can be dangerous to the health of the population as a result of direct contact with the dust, by inhalation of fine particulate matter and through food and water [4,10,11]. The monitoring of Pt, Pd, and Rh in surface waters, road dust, and roadside soil surfaces has therefore become increasingly important [1].

Spectroscopy instrumentation such as atomic absorption spectroscopy (AAS) [12,13], inductively coupled plasma optical emission spectroscopy (ICP-OES) [14], inductive coupled plasma mass spectroscopy (ICP-MS) [14,15], and neutron activation analysis (NAA) [16,17] was used for the total Pt, Pd, and Rh concentration in soil, dust, water, sediment, and biota samples. Inductively coupled plasma quadrupole mass spectrometry (ICP-QMS) seems to be one of the most promising spectroscopy techniques for Pt, Pd, and Rh determination at trace levels due to its ng/L range detection limits. It also offers the simultaneous determination of these platinum group metals (PGMs) in environmental samples [18–20].

On the other hand, electrochemical analysis has also been recognised as a powerful tool for the determination of the ng/L level of Pt, Pd and Rh in environmental samples [21–23]. In the determination of Pt, Pd and Rh, a large number of studies involve the use of a hanging mercury drop electrode (HDME) as the working electrode. A chronological comparison of the development of the current screen-printed sensor to other studies provided the following information on the improvement of the sensor produced in this study.

Almécija et al. [24] used a hanging mercury drop electrode (HMDE) sensor for the electroanalysis of only Rh in sediment samples that were collected near a motorway in close proximity to the Tagus Estuary (Lisbon, Portugal). The current study will focus on the application of a screen-printed carbon mercury free sensor, which will analyse Pt(II), Pd(II) and Pd(III) in roadside dust and soil samples.

The study of Orecchio and Amorello [25] focussed on the determination of Pt using differential pulse voltammetry in soil samples from Palermo (Italy). The voltammetric technique used involved differential pulse voltammetry. In comparison, the current study has a broader focus and will analyse for Pt(II), Pd(II) and Pd(III).

Dalvi et al. [26] showed that adsorptive stripping voltammetry using hexamethylene tetramine (HMTA) as the complexing agent was found to be highly sensitive method for the determination of Pt and Rh. Voltammetric measurements were performed using a hanging mercury drop electrode (HMDE) as the working electrode. In comparison, this current study will focus on the application of a screen-printed carbon mercury free sensor, which will lay the foundation for portable sensor development.

Svancara et al. [27] developed a procedure that employed a carbon paste electrode modified in situ with cationic surfactants of the quaternary ammonium salt type. It further involved a pre-concentration step that was based on a specific accumulation mechanism involving ion-pair formation. This sensor

enabled the detection of Pt(IV), Ir(III) and Os(IV). The detection was performed using cathodic scanning in the differential pulse voltammetric mode. This technique was based on a mercury-free sensor. In comparison, the current study will focus on the application of a screen-printed carbon mercury-free sensor, which will analyse Pt(II), Pd(II) and Pd(III) focusing on different analytes.

Galik et al. [28], developed another mercury-free sensor approach that allowed for the determination of osmium with a carbon paste electrode (CPE) modified with cationic surfactants of the quaternary ammonium salt type. The salts included cetyltrimethylammonium bromide (CTAB) and 1-(ethoxycarbonyl)-pentadecyltrimethyl-ammonium bromide (Septonex). Both salts were in situ and were employed for the pre-concentration of osmium (IV) via its hexachloroosmate(IV) anion. In comparison, the current study will focus on the application of a screen-printed carbon mercury-free sensor, which will analyse Pt(II), Pd(II) and Pd(III).

In the work by van der Horst et al. [29], a mercury-free glassy carbon sensor was developed using a bismuth film in the adsorptive differential pulse stripping voltammetric measurements of PGMs in the presence of dimethylglyoxime (DMG) as complexing agent. The current study will employ a bismuth-silver film screen-printed carbon electrode using differential pulse adsorptive stripping voltammetry for the detection of Pd(II), Pt(II) and Rh(III).

The research by Silwana et al. [30] showcased the development of a screen-printed mercury-free sensor where bismuth was coated on the screen-printed carbon electrode (SPCE) surface. The voltammetric procedure included pre-concentration of the metals using dimethylglyoxime (DMG) as the chelating agent, followed by adsorptive differential pulse stripping voltammetry (AdDPSV) at appropriate deposition potentials for Pd(II), Pt(II) and Rh(III). The authors improved the sensor development in the current study by developing a SPCE sensor with improved properties, such as more sensitive values for the limit of detection.

In the study by van der Horst et al. [31], a new generation of sensor development was showcased, using nanomaterials in the design and sensor construction. This study showcased the synthesis of bi-metallic bismuth-silver nanoparticles that can be incorporated into electrochemical sensor construction. No application to environmental samples was carried out at this developmental stage. The authors improved the sensor development in the current study by developing a SPCE sensor with improved properties, such as more sensitive values for the limit of detection.

Van der Horst et al. [32] continued the sensor development and incorporated the bi-metallic bismuth-silver nanoparticles in a glassy carbon electrochemical sensor. It was shown that a stripping voltammetric procedure for Pd(II), Pt(II) and Rh(III) determination was developed in the presence of dimethylglyoxime (DMG) as the chelating agent. The current study utilised the sensor properties from the above work and constructed a mercury-free sensor with more sensitive values for the limit of detection for Pd(II), Pt(II) and Rh(III).

The next step in the work of van der Horst et al. [33], focused on the development of a glassy carbon sensor and voltammetric procedure optimised for the simultaneous determination of Pd(II)-Rh(III) and Pt(II)-Rh(III) combinations, in the presence of dimethylglyoxime (DMG) as the chelating agent. No environmental samples were analysed at this stage. The current study will show an improved mercury free sensor, with the incorporation of the bi-metallic nanoparticles in a screen-printed carbon sensor with improved sensitivity.

The work of Van der Horst et al. [34], employed a screen-printed carbon electrochemical sensor to achieve more sensitive values for the limit of detection for Pd(II), Pt(II) and Rh(III). The sensor properties will be applied in the current study to show that the sensitivity of the sensor enabled greater improvement and application to environmental sample analysis to detect for Pd(II), Pt(II) and Rh(III) in roadside dust and soil samples.

In this study, the focus was on the environmental application of the sensor for the determination of Pt, Pd and Rh concentrations in road dust and roadside soil collected from roads outside Stellenbosch in the Western Cape, South Africa. Road dust and roadside soil samples were collected at each section of the road leading to a busy traffic light and intersection. The utility of ICP-QMS analysis and

bismuth-silver nanoparticles modified on screen-printed electrodes for the determination of Pt, Pd and Rh in environmental samples has been illustrated and discussed in this work. This study, therefore, want to showcase that a mercury-free screen-printed sensor was developed with the first utilisation of a bismuth-silver film screen-printed carbon electrode for the analysis of Pt(II), Pd(II) and Rh(III) in environmental dust and soil samples.

2. Materials and Methods

2.1. Dust and Soil Sampling

Roadside dust and soil samples were collected in the Western Cape Province at the Bottelary Road (BOT) close to Stellenbosch and at the Old Paarl Road (OP) close to Klapmuts, outside Stellenbosch (Figure 1). In this study four sampling points (~200 m apart) were identified on each section of the road leading to a busy traffic light and intersection. Dust and soil samples were taken in spring season, after most rain weather has stopped. The sampling points identified were on the left hand side on both roads (due to left-hand driving system in the country) and are indicated on the map in Figure 1. Approximately 100 cars pass the sampling sites in an hour, during the peak traffic times that are from 7:00 to 9:00 a.m. and 16:00 to 18:00, daily. The routes along the sampling sites also see both cars and small to medium trucks on the roads. The cars are used for traveling to work and the local university and schools, while the trucks are transporting agricultural goods to various destinations.

During sampling, clean handling techniques were employed throughout the roadside dust and soil sample collection to minimize the occurrence of cross-contamination and erroneous results [14]. In the collection of roadside dust samples, a nylon hand brush and plastic (high-density polyethylene) collection pan were used and dust were collected approximately 0.5 m away from the side of the road. The sampling sites were chosen to be between 100 and 400 m away from the traffic light, taking the safety of the researchers and the aim of the project into consideration.

(a)

Figure 1. *Cont.*
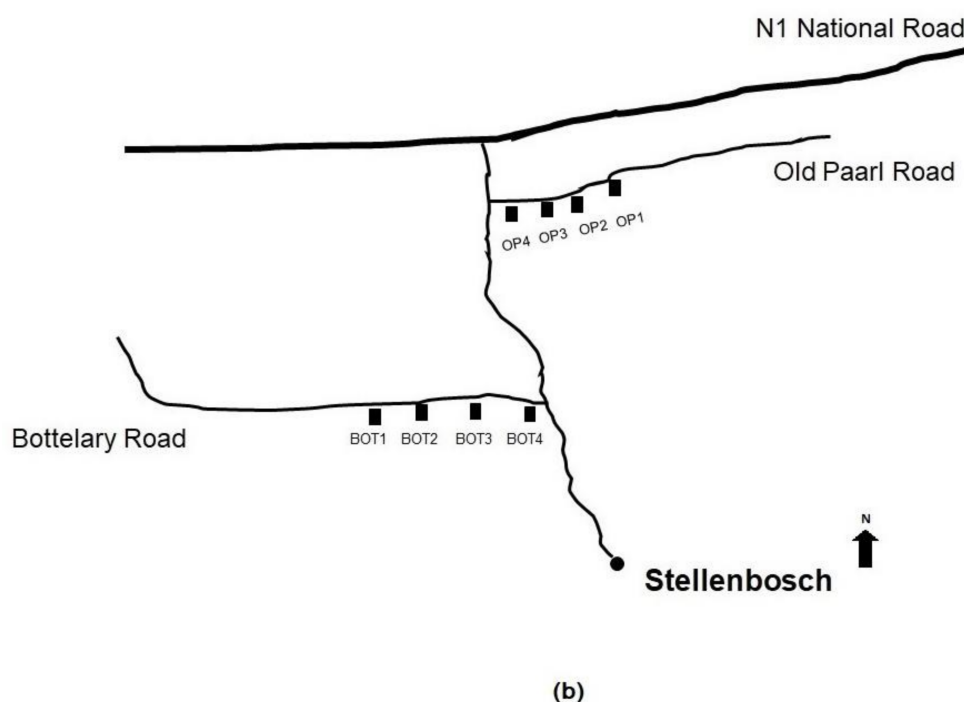
(b)
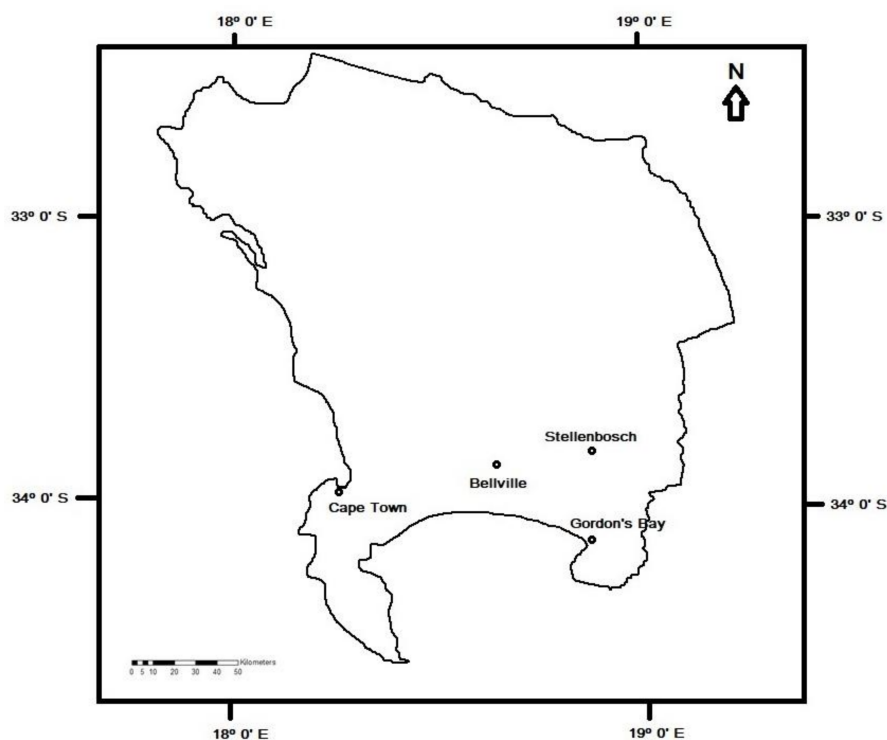
Figure 1. Map of the Cape Peninsula in the Western Cape, South Africa showing the location of the town Stellenbosch (in (**a**)) and the two main roads (in (**b**)) near the town where dust and soil samples were collected on the Old Paarl Road (OP) and Bottelary Road (BOT), respectively.

Each brush and pan was considered disposable and used only once. Roadside soil were collected by scooping up the surficial soil (0.1 cm depth) with a plastic trowel over 0.5 m^2 area and placed samples inside double Ziploc bags for the storage and transportation [35]. The samples were transported to the laboratory at Council for Scientific and Industrial Research (CSIR) (Stellenbosch, South Africa), where they were analyzed within 72 h.

2.2. Sample Preparation

The soil and dust samples were subjected to a chemical three-step sequential extraction procedure, to extract the organic matter-bound, carbonates-bound, and Fe-Mn oxides bound metal fractions. The three-step sequential extraction procedure by Li et al. [36] and Morera et al. [37] was selected with a slight modification of the extraction procedure (the exchangeable weakly-absorbed fraction not included), as shown in Table 1.

Table 1. Summary of the three-step sequential extraction procedure [38].

Fraction	Reactant	Conditions
Carbonate-bound	100 mL of 1.0 M NaOAc	Shaken for 5 h at room temperature
Fe-Mn oxide-bound	100 mL of 0.04 M NH_2OH-HCl	Shaken for 4 h at 85 °C
Organic matter-bound	20 mL of 0.02 M HNO_3 50 mL of 30% H_2O_2	Shaken for 4 h at room temperature

2.2.1. Carbonate-Bound

For the Carbonate-bound, approximately 6.25 g of roadside dust and soil samples were weighed out in polypropylene (PP) bottles and an aliquot of 100 mL of 1.0 M NaOAc (sodium acetate) solution was added to the dust and soil in the PP bottles. The mixture was shaken for 5 h at room temperature and then left standing for 30 min to allow the dust and soil to settle to the bottom. After 30 min the

aqueous solution was carefully decanted and pipetted into a beaker and then into a 100 mL PP bottle. The dust and soil fraction was carefully preserved in the PP bottles for use in the Fe-Mn Oxide-bound fraction extraction procedure. The sample was preserved with 1% (*v*/*v*) HNO$_3$ solution, and stored at 4 °C prior to analysis [36,37].

2.2.2. Fe-Mn Oxide-Bound

In the preparation of the Fe-Mn oxide-bound fraction a 0.04 M hydroxylamine hydrochloride (NH$_2$OH–HCl) was prepared in 25% acetic acid solution that was added to the same dust and soil samples weighed out in the PP bottles above. Approximately, 100 mL of aliquot of the above solution was added to the dust and soil samples in PP bottles. The mixture was shaken for 4 h at 85 °C in a water bath. After shaking it was left standing for 30 min to allow the dust and soil to settle to the bottom. The aqueous solution was carefully decanted and pipetted into a beaker and then into a 100 mL PP bottle. The dust and soil fraction was carefully preserved in the PP bottles for use in the organic-bound fraction extraction procedure. The sample was preserved with 1% (*v*/*v*) HNO$_3$ solution, and stored at 4 °C prior to analysis [36,37].

2.2.3. Organic Matter-Bound

For the Organic matter-bound, 0.02 M nitric acid (HNO$_3$) solution including a hydrogen peroxide (H$_2$O$_2$, 30%) was prepared and an aliquot of 20 mL of the 0.02 M HNO$_3$ solution and 50 mL of the H$_2$O$_2$, 30% solution was added to the dust and soil residue samples in the PP bottles. The mixture was shaken for 4 h at room temperature and then left standing for 30 min to allow the dust and soil to settle to the bottom. After 30 min the aqueous solution was carefully decanted and pipetted into a beaker and then into a 100 mL PP bottle. The solution was acidified and stored at 4 °C prior to analysis [36,37].

2.3. Platinum Group Metal Analysis

2.3.1. ICP-QMS Analysis

All equipment associated with the Inductively Coupled Plasma Quadrupole-based Mass Spectrometry (ICP-QMS) analysis was thoroughly cleaned with 0.5% *v*/*v* HCl solution and rinsed with deionized water (18.2 MΩ·cm @ 25 °C) before use, according to internationally recommended protocols [14]. The concentrations of total Pt, Pd, and Rh in the extracted solutions were determined by an Agilent 7500 series ICP-QMS equipped with Mass hunter software version G 7200 using the instrumental parameters shown in Table 2. The ICP-QMS experiments were performed at ambient temperatures (21 ± 2 °C) (Agilent Technologies, 7500 CX, Chemetrix, Midrand, South Africa) [1,14]. The extracted solutions obtained from dust and soil was filtered (cellulose acetate filters; pore size of 0.45 μm and diameter of 47 mm) and transfer into ICP-vials according to the requirements of the ICP-QMS being used. To the diluted extracted solution was spiked with a known amount of Pt, Pd and Rh prior to measurement. The ICP-QMS limits of detection were obtained by three times the standard deviation of ten replicate measurements divided by the slope of the calibration line, for the different blanks of Pt, Pd, and Rh, respectively. The ICP-QMS instrument was calibrated with solutions containing 0.01, 0.05, 0.10, 0.50, 1.0, 5.0, 10.0, and 20.0 ng/L of Pd, Pt, Rh prepared from standard solutions (diluted from 1000 ppm (99.99% purity) of Pd, or Pt or Rh; 0.2 M HCl; pH = 5). Samples were analyzed in triplicate. In this procedure the concentrations reported here were measured at μg/L levels. Detection limits for total ^{195}Pt, ^{105}Pd, and ^{103}Rh were 0.003, 0.003 and 0.001 μg/L, respectively.

Table 2. ICP-QMS operating conditions [1].

Instrument Parameter	Condition
Plasma power (W)	1590
Nebulizer gas flow (L/min)	0.98
Auxiliary gas flow (L/min)	0.11
Octapole bias (V)	−18
Quadrupole bias (V)	−17.2
Analytical Parameter	
Acquisition mode	He
Acquisition time	0.50 s for ^{103}Rh, ^{105}Pd, ^{195}Pt
Channels per mass	3 for ^{103}Rh, ^{105}Pd, ^{195}Pt
Number of repetitions/sample	3

ICP-QMS: inductively coupled plasma quadrupole mass spectrometry.

2.3.2. Voltammetric Analysis

The dust and soil extracted solutions were prepared separately for voltammetric analysis, by taking a 1 mL aliquot of each. To the 1 mL aliquot of extracted solutions, approximately 9 mL of 0.2 M sodium acetate buffer (pH = 4.7) solution, containing 0.5 µg/L Pt(II), Pd(II), and Rh(III) standard and 1×10^{-5} M dimethylglyoxime (DMG), was added, to give a final volume of 10 mL. The background voltammogram was recorded followed by the introduction of the Pt(II), Pd(II), and Rh(III) into the solution. All the differential pulse adsorptive stripping voltammetric (DPAdSV) experiments were performed in an oxygen environment and at room temperature [29,30,39].

The voltammetric determination of Pt(II), Pd(II), and Rh(III) in the extracted solutions was performed using a PalmSens® portable potentiostat/galvanostat, with the PalmSens trace program and accessories (PalmSens® Instruments BV, 3992 BZ Houten, The Netherlands). A portable potentiostat was connected to a microcomputer controlled by PS 2.1 software (PalmSens® Instruments BV, Houten, The Netherlands) for data acquisition and experimental control. The DPAdSV measurements were performed in a 20.0 mL conventional electrochemical cell. The screen-printed carbon electrodes with 4 mm diameter were purchase from Dropsens (Oviedo, Spain) and modified with bismuth-silver nanoparticles (SCPE/Bi-Ag) and used as the working electrodes [30,40,41].

According to Ntsendwana et al. [42] differential pulse voltammetry (DPV) has a high sensitivity and is used in electroanalytical chemistry as an effective technique when the concentration of an analyte is at ng/L range. In DPV methods important factors such as deposition potential (E_d) and deposition time (t_d) always influence the sensitivity and detection limit. The deposition potential and time was optimized to increase the electroanalytical performance of the Bi-Ag bimetallic nanosensor. The stability of the Bi-Ag bimetallic sensor was tested for the peak current over a period of 28 h. The bismuth-silver bimetallic nanosensor was practically applied by using the above optimized conditions for the determination of 1 ng/L of Pt(II), Pd(II) and Rh(III). For voltammetric analysis, the limits of detection ($\frac{3s}{m}$) were obtained by three times the standard deviation (s) of ten replicate measurements divided by the slope (m) of the calibration line, for the different blanks of Pt, Pd and Rh, respectively.

In differential pulse adsorptive stripping voltammetry it is important to study the effect of interferences because some trace metals can interfere with the detection of PGMs. These metals can complex competitively with the chelating agent (DMG) and then absorbed competitively onto the Bi-Ag bimetallic sensor surface. These interference effects produce signals close to that of the different PGMs and completely suppress the PGMs peaks. Only the metal ions such as Na(I), Fe(III), Ni(II), Co(II) that could potentially interfere with these PGMs were investigated. Also, the phosphates and sulphates were studied in model solutions with concentrations of 1 ng/L of these interfering ions. These ions were chosen because they reasonably co-exist in real freshwater samples, and are thus expected to exhibit redox activity at the SPCE/Bi-AgF nanosensor surface. In the present study the

determination of Pt(II), Pd(II) and Rh(III) was done in 0.2 M acetate buffer (pH = 4.7) solution at the surface of a SPC/Bi-AgFE nanosensor.

In this study the optimized working conditions for the determination of a series of standard solutions of Pt(II), Pd(II) and Rh(III) metal ions using DPAdSV are summarized in Table 3. The working conditions in Table 3 shown that Pd(II) and Rh(III) have different deposition potentials with the same deposition time. Important optimized working conditions such as supporting electrolyte, chelating agent (dimethylglyoxime, DMG) concentration, and potential window was the same value throughout the study for Pt(II), Pd(II) and Rh(III). The optimum deposition potential and deposition time was obtained by scanning the sensor from -0.3 to -1.2 V and 30 s to 240 s in a 1 ng/L solution of Pt(II), Pd(II) and Rh(III), respectively. Under the optimized conditions using the SPC/Bi-AgFE nanosensor the LODs of Pt(II), Ps(II) and Rh(III) was 6×10^{-5} µg/L for Pt(II), 7×10^{-5} µg/g for Pd(II) and 2×10^{-4} µg/g for Rh(III), respectively.

Table 3. Summary of the DPAdSV optimum conditions for the determination of Pt(II), Pd(II), and Rh(III) [43].

Stripping Step	Determinant	[1]Pt(HDMG)$_2$	[2]Pd(HDMG)$_2$	[3]Rh(HDMG)$_3$
	pH		4.7	
	Reduction potential (V)	-0.9	-0.7	-0.8
	Deposition time (s)	30	90	30
	Supporting electrolyte		0.2 M NaOAc	
Measurement Technique	**Measurement**		**DPSV**	
	Potential window		0.1 to -0.6 V	
	Supporting electrolyte		0.2 M NaOAc	

[1]Pd(HDMG)$_2$: Palladium-dimethylglyoxime complex. [2]Pt(HDMG)$_2$: Platinum-dimethylglyoxime complex. [3]Rh(HDMG)$_3$: Rhodium-dimethylglyoxime complex. DPAdSV: differential pulse adsorptive stripping voltammetry. DPSV: differential pulse stripping voltammetry.

3. Results

3.1. Spectroscopic Analysis

In spectroscopic analysis of Pt, Pd, and Rh is associated with numerous interference problems. According to Gomez et al. [44] spectroscopic interferences, due to the formation of argides e.g., complicate PGMs determination in environmental samples. In this study the isotopes [195]Pt, [105]Pd and [103]Rh were used to determine Pt, Pd, and Rh concentrations, respectively, in the samples because of their high natural abundances and because they are subject to fewer interferences. It should be noted that the total concentrations of Pt, Pd, and Rh in the soil and dust samples were determined with ICP-QMS analysis, since the technique was not set-up to determine the different oxidation states of Pt, Pd, and Rh during this analysis.

3.1.1. Road Dust

Figure 2 shows the mean concentrations and standard deviations of Pt, Pd and Rh in road dusts and roadside soil from Bottelary Road (BOT) and Old Paarl Road (OP) roads in the Western Cape, South Africa, respectively. In Figure 2a the results obtained for the road dust samples are shown with concentrations range from 0.16 ± 0.06 to 1.28 ± 0.06 ng/g (dry weight (d.wt)) for Pt, 0.64 ± 0.06 to 1.76 ± 0.05 ng/g dry weight (d.wt) for Pd and 0.064 ± 0.02 to 0.8 ± 0.04 ng/g (d.wt). The results shown in Figure 2a also indicate that there was a difference in Pt, Pd and Rh contamination levels in the dust samples. Palladium was the major contaminant found at every sampling location. The results indicate that concentrations of Pt, Pd, and Rh are in the order of Pd >Pt >Rh distributions on both roads. The highest concentration of Pt, Pd, and Rh at both sampling locations was at the sampling sites closest to the traffic lights and the lowest concentrations about 400 m away from the traffic lights.
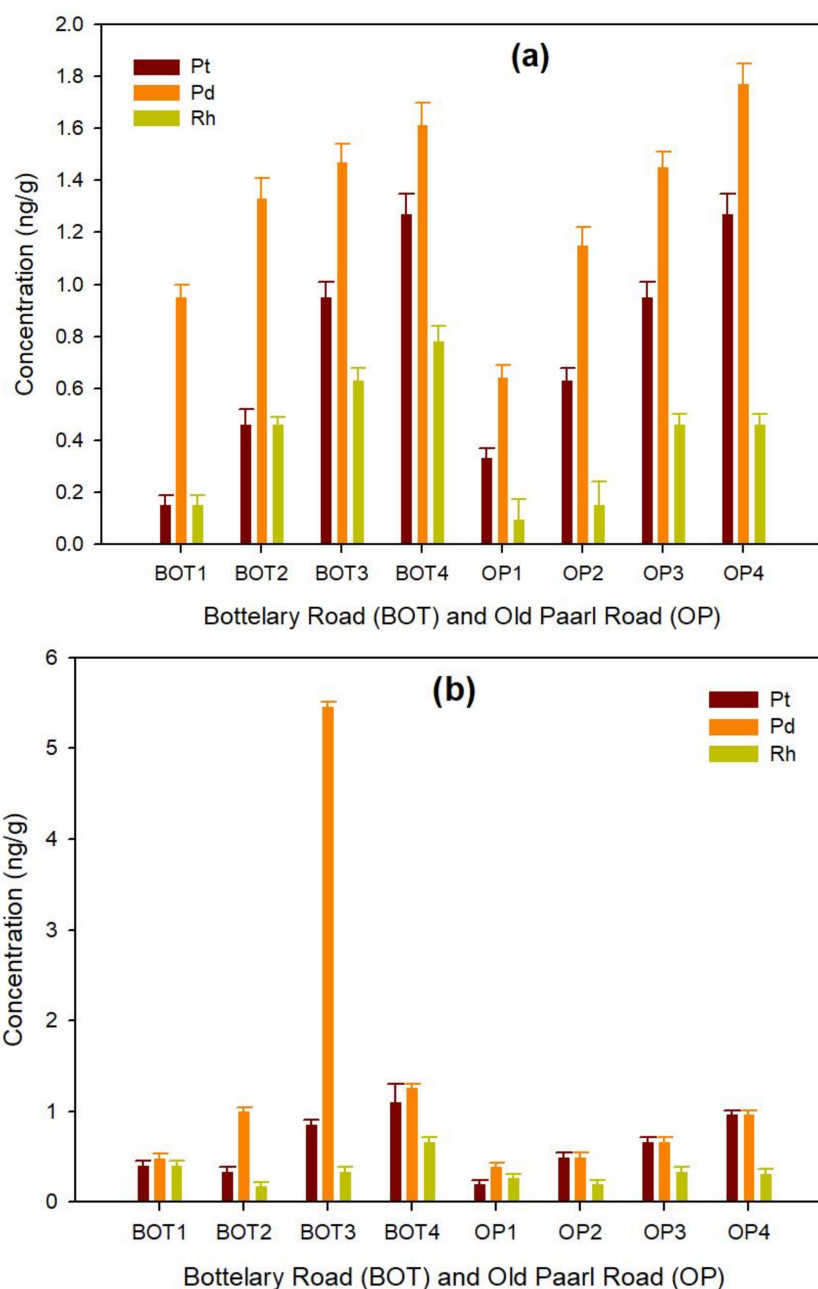
Figure 2. ICP-QMS results for Pt, Pd, and Rh concentrations in roads dust (**a**) and roadside soil (**b**) samples on Bottelary Road (BOT) and Old Paarl Road (OP).

3.1.2. Roadside Soil

Figure 2b shows the mean concentrations and standard deviations of Pd, Pt, and Rh in the soil samples collected from Bottelary and Old Paarl Roads. The range of Pt, Pd, and Rh concentrations in the soil samples was from 0.06 ± 0.02 to 1.12 ± 0.05 ng/g (d.wt) for Pt, 0.48 ± 0.05 to 5.44 ± 0.11 ng/g (d.wt) for Pd and 0.08 ± 0.04 to 0.64 ± 0.05 ng/g (d.wt) for Rh at Bottelary Road. Similarly, the concentrations was 0.16 ± 0.04 to 0.96 ± 0.04 ng/g (d.wt) for Pt, 0.32 ± 0.05 to 0.96 ± 0.07 ng/g (d.wt) for Pd and 0.032 ± 0.02 to 0.32 ± 0.04 ng/g (d.wt) for Rh at Old Paarl Road, respectively. The highest concentration of Pd was found to be 5.44 ng/g (d.wt) in sample BOT3. In the case of Pt, the highest concentration was found to be 1.12 ng/g (d.wt) in sample BOT4, indicating that the Pt, Pd and Rh concentrations are higher in roadside soil samples at the Bottelary Road location. The concentration

level of Pt, Pd and Rh appeared to be in the following order in the soil samples obtained by ICP-QMS analysis of the Bottelary Road samples, Pd >Pt >Rh distribution.

In the case of the Old Paarl Road samples, Pt, Pd and Rh distribution in the samples was found to be in the order Pd (5.44 ng/g) >Pt (1.12 ng/g) >Rh (0.64 ng/g). The results observed in both road dust and roadside soil samples indicate that there is a widespread shift in the development of catalytic converter technology away from Pt towards Pd as the main catalytic component [35]. The mean Pt, Pd and Rh concentrations in the dust and soil samples at the two study areas are lower to those from Scotland (13–335 ng/g) [45], Rome, Italy (14.4–62.2 ng/g) [46], Bialystok, Poland [47], Perth, Australia (8.8–91.4 ng/g) [35], and Goteborg, Sweden (80.0 ng/g) [48].

3.2. Voltammetric Analysis

Differential pulse adsorptive stripping voltammetric behaviour of Pt(II), Pd(II) and Rh(III) on a screen-printed carbon / bismuth-silver film electrode (SPC/Bi-AgF) sensor was evaluated in terms of the influence of stripping parameters such as dimethylglyoxime chelating agent concentration, deposition potential and deposition time. Finally, the results of the optimised parameters were tabulated and the influence of various metal ions as potential interference compounds on the determination of Pt(II), Pd(II), and Rh(III) ions was studied under experimental conditions illustrated in Table 3.

It was found that the Pt(II), Pd(II), and Rh(III) peak current intensities decreased only slightly for the Bi-Ag bimetallic nanosensor over the time period, indicating good stability for the nanosensor (voltammograms not shown). The behaviour of Pt(II), Pd(II), and Rh(III) was investigated at 0.5 to 1.5 ng/L concentrations in the presence of Co(II), Cd(II), Ni(II), Pb(II), Fe(III), and Na^+. This study showed that these ions did not interfere with the determination of Pt(II), Pd(II) and Rh(III). For each metal, a linear relationship was observed between peak current and concentration ranging from 2×10^{-4} to 8×10^{-4} ng/g (Pt(II)), 4×10^{-4} to 1×10^{-3} ng/g (Pd(II)) and 2×10^{-4} to 8×10^{-4} ng/g (Rh(III)). The linear response and the equation of the linear calibration curves are $y = 0.690x + 0.718$ for Pt(II), $y = 0.773x + 0.615$ for Pd(II) and $y = 3.953x + 0.580$ for Rh(III), with correlation coefficients of 0.988, 0.991 and 0.970, respectively.

3.2.1. Road Dust

Figure 3a shows the mean concentrations and standard deviations of Pt(II), Pd(II) and Rh(III) in road dusts from Bottelary Road and Old Paarl Road in the Western Cape, respectively. The range of Pt, Pd and Rh concentrations in the road dust samples was found to be 8.96 ± 1.83 to 26.88 ± 2.14 pg/g (d.wt) for Pt(II), 58.88 ± 1.99 to 69.28 ± 2.28 pg/g (d.wt) for Pd(II) and 29.92 ± 3.29 to 202.88 ± 4.23 pg/g (d.wt) for Rh(III) at the Bottelary Road sampling sites. Similarly, the Pt, Pd and Rh concentrations was found to be 24.64 ± 3.07 to 140.48 ± 3.26 pg/g (d.wt) for Pt(II), 40.96 ± 2.50 to 68.64 ± 3.15 pg/g (d.wt) for Pd(II) and 11.36 ± 2.57 to 29.12 ± 2.25 pg/g (d.wt) for Rh(III) at the Old Paarl Road sampling sites.
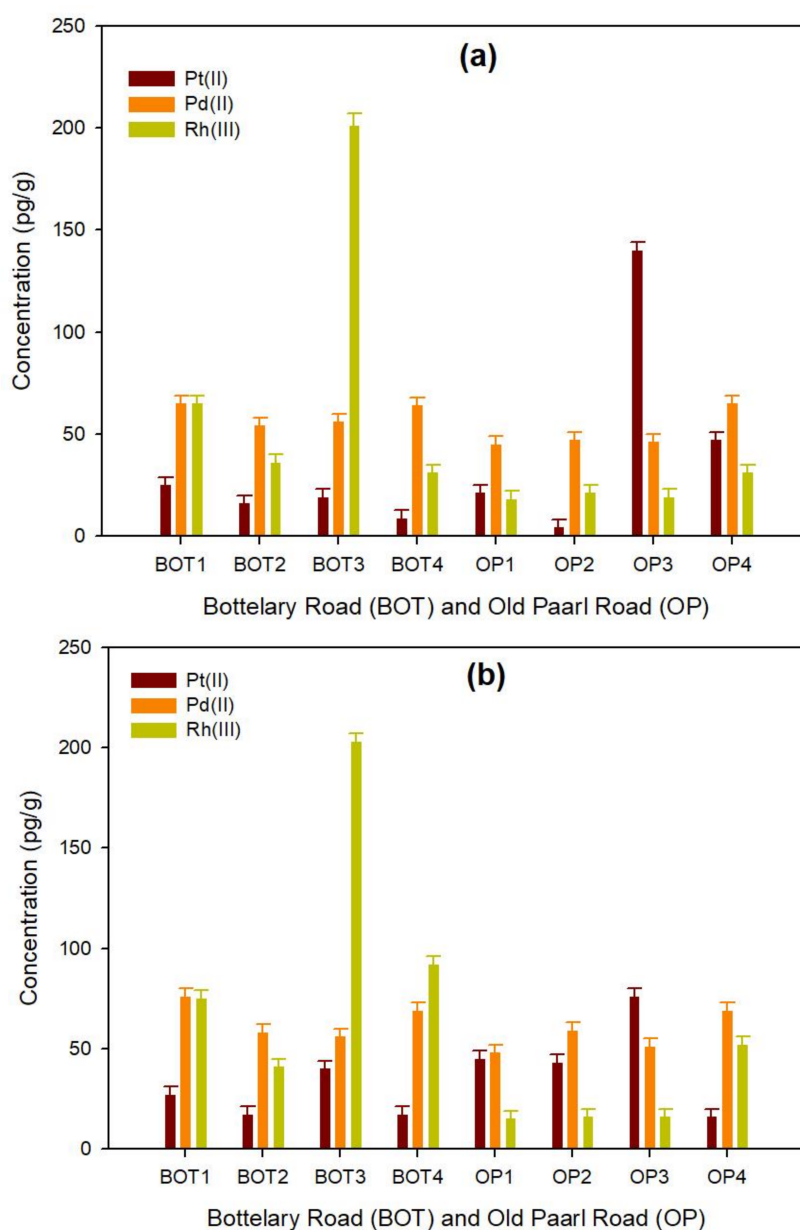
Figure 3. DPAdSV (differential pulse adsorptive stripping voltammetric) results for Pt, Pd, and Rh concentrations in road dust (**a**) and roadside soil (**b**) samples on Bottelary Road (BOT) and Old Paarl Road (OP).

Analysis of the results have shown that Pd(II) was the major contaminant in dust and soil at most of the sampling sites on both the Bottelary and Old Paarl Roads. This was followed by Pt(II) concentration, which was higher than the Pd(II) concentration at sampling site OP3 only. The results obtained in Figure 3a further showed various trends in PGMs contamination levels in the road dust samples at all the sampling sites.

3.2.2. Roadside Soil

Figure 3b illustrates the results obtained for the mean concentrations and standard deviations of Pt(II), Pd(II) and Rh(III) in roadside soil from Bottelary and Old Paarl Roads, respectively. The SPC/Bi-AgFE sensor showed greater results for Rh(III) at Bottelary and Pd(II) at Old Paarl Roads, respectively. The Pt(II), Pd(II) and Rh(III) concentrations in the roadside soil was found to be 18.88 ± 1.74 to 37.60 ± 1.68 pg/g (d.wt) for Pt(II), 56.80 ± 2.26 to 77.92 ± 2.55 pg/g (d.wt) for Pd(II)

and 38.66 ± 5.06 to 203.90 ± 3.29 pg/g (d.wt) for Rh(III) at the Bottelary Road sampling sites. Similarly, the Pt(II), Pd(II) and Rh(III) concentrations are 17.28 ± 3.12 to 81.44 ± 3.07 pg/g (d.wt) for Pt(II), 45.12 ± 3.46 to 72.48 ± 1.35 pg/g (d.wt) for Pd(II) and 14.34 ± 3.08 to 53.35 ± 4.07 pg/g (d.wt) for Rh(III) at the Old Paarl Road sampling sites. The highest concentration of Rh(III) is 203.90 pg/g (d.wt) at sample site BOT3. In the case of Pd(II), the highest concentration is 77.92 pg/g (d.wt) at sample site BOT1. Furthermore, the Pt(II), Pd(II) and Rh(III) concentrations measured at Bottelary Road are greater than the Pt(II), Pd(II) and Rh(III) concentrations obtained at Old Paarl Road in roadside soil samples.

The above results therefore indicate that Pd concentrations measured at all the sampling sites using ICP-QMS were much higher than Pt and Rh concentrations. In the case of DPAdSV analysis both Pd(II) and Rh(III) concentrations was the highest at most of the sampling sites. Table 4 further illustrates the comparison of obtained results (DPAdSV and ICP-QMS) in present study with ICP-MS and DPAdSV results from other studies. It was observed that this study revealed similar low limits of detection, a highly comparable linear response range and faster response time for Pt, Pd and Rh analysis in soil and dust samples.

Table 4. Comparison of the limit of detection (LOD) values for the DPAdSV and ICP-QMS results obtained for the determination of Pt, Pd, and Rh concentrations in environmental samples.

Method	Pollutant	Sample	Linear Response	LOD	References
ICP-MS	Pd Pt Rh	Road dust	2.70–203.7 ng/g 8.1–118.5 ng/g 1.2–54.8 ng/g		[49]
HR-ICP-MS	Pd Pt Rh	Roadside soil	0.3−17 ng/g 1.1−58 ng/g 0.07−8.2 ng/g	0.1 ng/g 0.7 ng/g 0.04 ng/g	[50]
ICP-MS	Pt	Road dust		12.0 ng/mL	[35]
DPAdSV	Pd(II) Pt(II) Rh(III)	Road dust Roadside soil	0.2–1.0 ng/L 0.2–1.0 ng/L 0.4–1.0 ng/L	0.19 ng/L 0.20 ng/L 0.22 ng/L	[31]
ICP-MS	Pd Pt Rh	Soil		0.088 μg/L 0.043 μg/L 0.016 μg/L	[51]
ICP-MS	Pt	Soil		7.6 ng/L	[52]
DPAdSV	Pt(II)		6.0–54 pg/L	6.0 pg/L	[53]
ICP-QMS	Pd Pt Rh	Road dust Roadside soil		3×10^{-6} μg/g 3×10^{-6} μg/g 1×10^{-6} μg/g	This work
DPAdSV	Pd(II) Pt(II) Rh(III)	Road dust Roadside soil	4×10^{-7}–1.0×10^{-6} μg/g 2×10^{-7}–8×10^{-7} μg/g 2×10^{-7}–8×10^{-7} μg/g	7×10^{-8} μg/g 6×10^{-8} μg/g 2×10^{-7} μg/g	This work

ICP-MS: inductive coupled plasma mass spectroscopy. HR-ICP-MS: high resolution inductive coupled plasma mass spectroscopy.

3.3. Discussion

3.3.1. Mobility of Pt, Pd, and Rh in Roadside Dust and Soil Samples

This study evaluated fate and transport of three precious metal concentrations (Pt, Pd, and Rh) in roadside soil and dust samples, with the focus on establishing whether the motor vehicle catalytic converter is the source from which these metals originate. Secondly, to compare the voltammetric determination of Pt, Pd, and Rh in roadside soil and dust samples, to the spectroscopic determination of these metals using spectroscopy.

The correlations between the Pt, Pd, and Rh in the dust and soil samples were evaluated to determine if the vehicular traffic is the main source of Pt, Pd and Rh into the environment. This was done by calculating the ratio of the Rh to Pt, Pd-Pt and Pd-Rd for the concentrations analysed and reporting the R^2 value of the trendline of the plots analyzed. The sampling sites on the Bottelary Road (BOT1–BOT4) are in close proximity to the traffic light at the main intersection, with all cars into the Stellenbosch town area stopping there.

In the case of the dust samples, the ratio for Rh-Pt, Pd-Pt and Pd-Rd were found to be 0.9411, 0.9498 and 0.9477, respectively. These ratios are positive with little variation, indicating that the anthropogenic inputs are vehicular traffic in the sampling location contributing to the concentration of Pt, Pd and Rh in the dust samples.

For the Old Paarl road sampling sites (OP1–OP4), the dust samples showed ratios for Rh-Pt, Pd-Pt and Pd-Rd of 0.9764, 0.8993 and 0.8767, respectively. The results confirmed the vehicular traffic contribution, but for the sampling site it was also found that a weaker relationship exist between Pd-Pt and Pd-Rd. The contributing factors should be the focus of a future study.

Evaluation of the correlations between the Pt, Pd and Rh concentrations in the soil samples for the Bottelary Road sites have shown correlations for Rh-Pt, Pd-Pt and Pd-Rd of 0.908, 0.2024 and 0.2053, respectively. These results reported weaker relationships for the Pd-Pt and Pd-Rd ratios, which may be indicative of the dust not settling into the soil immediately, or other anthropogenic factors are at play.

For the Old Paarl road sampling sites (OP1–OP4), the dust samples showed ratios for Rh-Pt, Pd-Pt and Pd-Rd of 0.942, 0.9331 and 0.8271, respectively. The results showed a stronger relationship for vehicular contribution to the Pt, Pd and Rh concentrations in the soil samples, when compared to the results for the Bottelary Road sites.

3.3.2. Comparison between Spectroscopic and Voltammetric Analysis

Secondly, the study wanted to establish whether the voltammetric determination of Pt, Pd and Rh provides an alternative analytical technique to ICP-QMS spectroscopy, for the determination of these Pt, Pd and Rh concentrations in roadside soil and dust samples. The results have confirmed the appropriateness and usefulness of both spectroscopic and voltammetric techniques for the determination of Pt, Pd and Rh concentrations in environmental samples. Spectroscopy offered the simultaneous analysis of Pt, Pd and Rh in the environmental samples, while voltammetric analysis allowed some speciation for the determination of Pd(II), Pt(II) and Rh(III) species in the environmental samples. Therefore, depending on the objective of the research project, there is room for both types of analysis of Pt, Pd and Rh concentrations. The results obtained showed very sensitive limit of detection (LOD) values for both techniques, but voltammetric analysis further delivered a higher sensitivity and faster response time for PGMs analysis in soil and dust samples. This study has also showed the novel application of a SPC/Bi-AgFE sensor for the voltammetric determination of Pd(II), Pt(II) and Rh(III) in soil and dust samples.

4. Conclusions

The construction, optimization and practical application of the two methods (ICP-QMS and DPAdSV) have been presented for the analysis of Pt, Pd, and Rh concentrations in roadside soil and dust samples. Road dust and roadside soil samples, collected from the Bottelary and Old Paarl Roads near Stellenbosch in the Western Cape Province were used to determine the Pt, Pd, and Rh concentrations and to illustrate the practical application of the developed methods. The proposed methods include advantages of high selectivity, high sensitivity, speed and simplicity. The results have therefore shown that the Pt, Pd, and Rh concentrations studied by the two methods showed low concentration in the dust and soil samples collected at Bottelary and Old Paarl Roads.

The results obtained have shown that there is room for both spectroscopy and voltammetric analysis of Pt, Pd and Rh in environmental dust and soil samples. Spectroscopy offers the luxury of low detection limits and simultaneous determination of Pt, Pd and Rh in environmental samples.

Spectroscopic analysis remains a trusted technique for the analysis of environmental sample, but voltammetric analysis offers an alternative or complimentary technique and speciation of the metal ions. This study reported the first utilization of a bismuth-silver film screen-printed carbon electrode (SPCE) for the analysis of Pt(II), Pd(II), and Rh(III) in environmental dust and soil sample analysis. The results obtained have shown that SPCE technology is advancing towards another set of metals that can be measured with a portable electrochemical instrument. Incorporating the SPCE/Bi-Ag sensor showcased in this study in a portable potentiostat, already available on the market, environmental analysis can be performed in the terrestrial and aquatic environment and allow the on-site analysis of these metal ions.

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