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Chapter 2

Graphene Oxide–Antimony Nanocomposite Sensor for Analysis of Platinum Group Metals in Roadside Soil Samples

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Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/67699

Abstract

The present study introduced a very sensitive and low-cost analytical procedure based on voltammetry to study platinum group metals in road dust and roadside soil matrices. Cathodic stripping voltammetry in conjunction with a reduced graphene oxide-antimony nanocomposite sensor and ICP-MS analysis were used to analyse roadside soil and dust samples. The results were processed to evaluate possible pollution in order to map the distribution of the PGMs along specific roads in the Stellenbosch area, outside Cape Town. The results revealed that within each site under investigation, Pd was more abundant than Pt and Rh using both voltammetric and spectroscopic methods. The AdDPCSV results obtained showed concentrations for Pd(II) ranging between 0.92 – 4.0 ng kg^{-1}. For Pt (II), the concentrations ranged between 0.84 – 0.99 ng kg^{-1}. For Rh(III), concentrations ranged between 0.42 – 1.21 ng kg^{-1}. The ICP-MS results showed Pd concentrations ranging between 0.01 – 0.34 μg kg^{-1}. For Pt the concentrations ranged between 0.004 – 0.07 μg kg^{-1}. For Rh, concentrations ranged between 0.002 – 0.26 μg kg^{-1}. The analysis showed significant levels of all PGMs in soil and dust samples analysed. Metal concentration in dust and soil followed the trend Pd > Pt > Rh using both voltammetric and spectroscopic techniques.

Keywords: adsorptive stripping voltammetry, roadside dust and soil samples, ICP-MS analysis, PGMs, Sensitivity, speciation

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1. Introduction

The pollutants present in soil not only affect the micro-flora and fauna of soil ecosystems but also contaminate fruits and vegetables in close vicinity. They result in formation of leachates that ultimately contaminate the ground water passing through the soil profiles or by directly entering the surface water system through run off. The consumption of the contaminated food and water causes severe health problems in human beings [1].

Research has shown that platinum group metals (PGMs) could become available to plants and especially to humans and livestock, who consume plants growing on a contaminated soil [2]. In general the Pt(II), Pt(V) and Pd(II) toxic effects on the cellular level are comparable to the toxic effects of Cd(II) and Cr(VI), sometimes even exceeding the damage induced by the above species of Cd and Cr [3].

Numerous studies have concentrated on the heavy metal (e.g. Pb or Cd) concentrations in the environment, while relatively few studies have focussed on PGMs in the environment [4–7]. PGMs released from the catalytic converters are primarily bound to aluminium oxide particles [8–9]. Until recently, they were regarded as inert elements, but studies have shown that they may be soluble and quite reactive. High levels of PGMs in human body may cause asthma, nausea, hair loss, abortion, dermatitis and other health problems [10].

PGMs are emitted both in nanometre and micrometre particle sizes on the surfaces of road dusts, roadside soils and plants during vehicle operation as evidenced by atmospheric particle analysis, but their presence is increasing as a consequence of the use of catalytic converters introduced to reduce gaseous automobile emissions [11–14].

Studies conducted by Barbante et al. [15] showed that the spread of PGMs in the environment is rather a global process, despite some works asserting the low transportability of these pollutants. Therefore, it is important to study how these PGMs species may become chemically/biochemically active and mobile in interactions with various environmental matrices under the changing weather conditions, in order to give a prediction on the possible hazards of PGMs for human health.

PGMs contamination initially occurs in airborne particulate matter (PM), roadside dust, soil, sludge and water, etc., which finally results in uptake and bioaccumulation of these elements in the living organisms. The high demand for on-site monitoring of these metals in environmental matrices has attracted much attention from researchers since the concentration is still very low at present [16]. Moreover, in samples of complex composition, the determination of these elements is still a special challenge to trace element analysis [17–19].

There is a need for dynamic analytical techniques able to routinely measure parameters that are reliable predictors of bio-availability and bio-uptake and, thus of the potential ecotoxicological risk [20]. Ideally such measurements should be made *in situ* to avoid sampling and sample handling artefacts. This is a considerable challenge, techniques must be sufficiently robust to withstand field deployment, provide adequate sensitivity and furnish a signal that can be quantitatively interpreted in terms of chemical species present [20].

http://dx.doi.org/10.5772/67699

The measurements of total metal concentrations alone do not yield sufficient information on the ecotoxicological impact and fate of metallic elements. The measurement of specific species or groups of homologous species is therefore essential. The major existing techniques for trace-metals analyses are spectroscopic (in particular, graphite furnace atomic absorption spectroscopy (GF-AAS) and inductively coupled plasma mass spectroscopy (ICP-MS), neutron activation analysis (NAA) and voltammetric and chronopotentiometric analysis) [21].

Briefly, the advantage of NAA, GF-AAS and ICP-MS compared to voltammetric techniques is that they are applicable to a large number of elements. Their major drawbacks are their much higher cost and, above all, the fact that they allow measurements of total concentration only. Consequently, speciation measurements, using these detection techniques, are feasible only by coupling them with separation and extraction procedures. However, such steps significantly increase the risk of contaminations or chemical species modifications during sample storage or sample handling, and dramatically increase the cost of analyses. This is a major barrier to their application to routine speciation measurements on large sample sets, even though it would be the only means to interpret correctly the environmental impact of metals [21].

In contrast, the characteristics of voltammetric techniques make them particularly well suited for automatic (thus low cost) *in situ* speciation measurements, with no or minimum sample change, i.e., under conditions that dramatically minimize contaminations by reagents or losses by adsorption on containers. It has some intrinsic advantageous features like quick analysis speed, high precision and accuracy, relatively portable and inexpensive instrumentations and can be used 'on-site' measurements, biomedical, environmental and industrial applications [22–24].

The main objective of this work was aimed to apply ICP-MS analysis and to evaluate and compare the established simple method for analysis of road dust and roadside soil samples, with a voltammetric technique. Numerous studies of PGMs have been done in South Africa using ICP analysis and focusing on Pt analysis [25]. The only PGMs studies with stripping voltammetry data have been reported by van der Horst et al. [26]. This study supplied baseline information to enable future studies and detection of PGMs in soil and dust samples. Accordingly, since catalytic car converters may increasingly contribute as a main source of these environmental pollutants. Hence, there was a need for the present study so as to compare the concentrations of PGMs with studies in other parts of the world to ascertain the impact of catalytic car converters on environment quality. Furthermore, this work is also a contribution to the monitoring of PGMs in the South African environment since very little is known about the influence of these elements on organisms exposed to this type of contamination.

2. Experimental

2.1. Study area and site description

The study was conducted on the analysis of road dust and roadside soil samples, collected on busy roads of the Stellenbosch area in the Western Cape Province (South Africa). Soil and

dust samples were collected on the Bottelary road that joins the R304 road into Stellenbosch (**Figure 1**). Sampling sites and corresponding samples collected on the Bottelary Road were labelled BOT1 to BOT4. A second set of samples were collected at sampling sites on the Old Paarl road that joins the R44 (or Adam Tas Road) that also runs into Stellenbosch. These sampling sites and corresponding samples were labelled OP1 to OP4 (**Figure 1**).

The overall sampling sites were categorized based on the level of traffic flow. **Figure 1** represents a schematic map of the study area and the sampling points.

2.2. Sample collection

Samples of soil and dust were collected from the eight sampling locations highlighted (**Figure 1**), by demarcating a square segment of about 10 cm^2 in the top soil. The grass on the top of some soil samples was removed, while the soil around the grassroots was shaken off to form part of the sample collected.

To avoid contamination during the collection and processing of sample material, nitrile gloves were worn at all times. It was hypothesised that soil and dust inputs from the surrounding area would be a primary source of particulates containing PGMs to settle on road surfaces. The OP sites are categorized as high-traffic zones. Site OP4 and BOT4 are the junctions that receive heavy traffic from R44 to R304, respectively. All sampling devices were cleaned by rinsing with pure water, 25% HNO_3 and 10% HCl, followed by drying for several days before sampling. Road dust and roadside soil were collected using hand auger and brush.

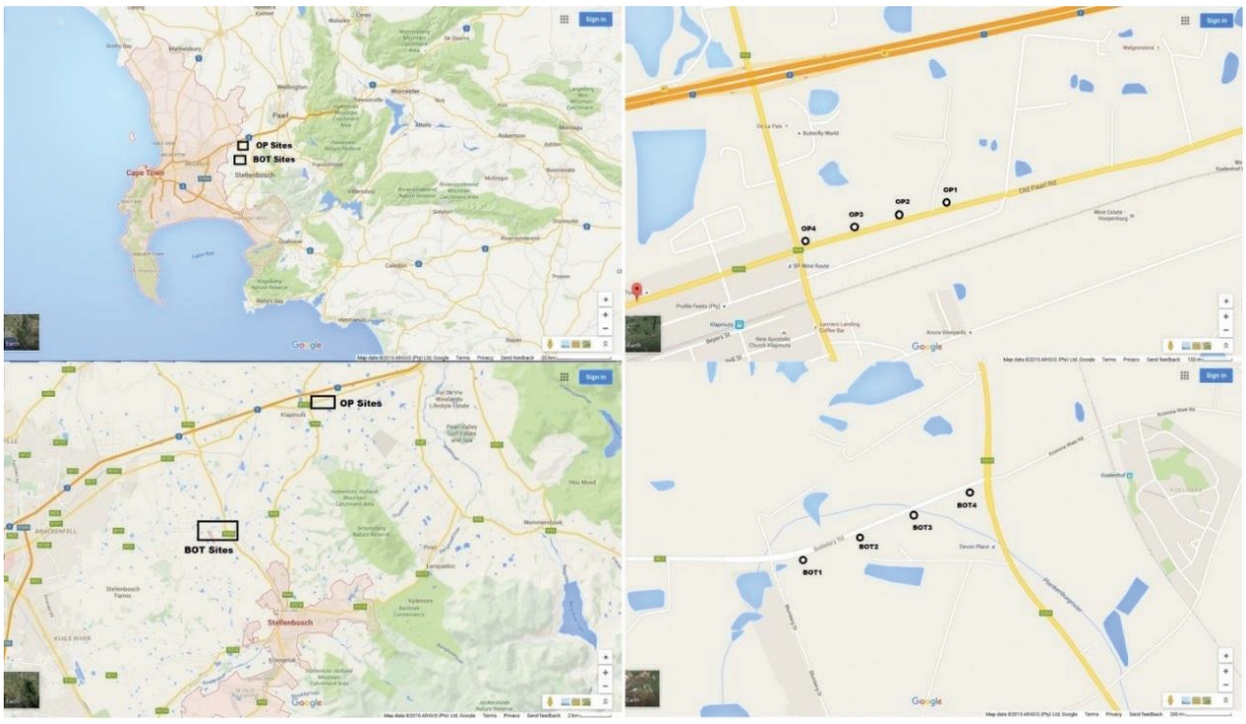


Figure 1. Schematic map of the study area near Stellenbosch (outside Cape Town), showing the sampling sites on Bottelary and Old Paarl Roads.

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The samples were placed into double zip-locked plastic bags labelled BOT1–BOT4, OP1–OP4 to represent Bottelary and Old Paarl sites, respectively. The samples were transported to the laboratory on ice and transferred to clean storage containers, before drying was done. Soil samples were air-dried, grinded using mortar and pestle, and then sieved through a 1-mm mesh sieve to remove debris and small stones. The samples were then transferred into a zip-lock bag and stored in the fridge at 4°C until analysis. The working environment was also kept clean to avoid any cross-contamination [27].

2.3. Reagents

All chemical reagents used for calibration plots and design of electrodes were of analytical grades purchased from Aldrich (Germany). All other reagents used were provided by Merck (South Africa) and included sodium acetate, ammonia with a purity of ca. 25% ammonium chloride, hydrochloric acid (purity 32%) and nitric acid (purity 55%). Glacial acetic acid and ethanol (95%) were purchased from Kimix (South Africa). The electro-analytical measurements were performed in 0.2 M sodium acetate buffer (pH = 5.2) solution and a MilliQ deionized water (resistivity of 18.2 MΩ cm) was used for the preparation of the reagent solutions.

2.4. Instrumentation and analysis

In most inorganic analytical laboratories, PGMs analysis is usually performed using inductively coupled plasma-mass spectroscopy (ICP-MS). For the purpose of this study, both voltammetric and ICP-MS techniques were used. The two techniques were used to compare results, considering aspects of both analytical and technical details. These analytical techniques differ in terms of sensitivity, requirements for sample preparation and costs of analysis [28].

Voltammetry is, however, better than spectroscopy in terms of interferences and because it does not require addition of matrix modifiers. It is, also, certainly much less expensive. Finally, with regard to analysis time voltammetry is more advantageous [28]. In addition the detection limits of stripping voltammetry are better than those of ICP-MS analysis. Comparison of the two techniques is shown in **Table 1**.

2.4.1. Sequential extraction

Since the total concentration does not yield information on mobility, origin or bioavailability of metallic elements, metals in sediments have to be associated with the different fractions present. For soils and sediments the term speciation refers to the process of identification and quantification of metals in phases, such as carbonates, oxides, organic matter and others, which may be extracted in sequence [35].

All materials associated with the metal extraction were thoroughly acid-cleaned and rinsed with deionised water before use, according to internationally recommended protocols [36]. A schematic presentation of the extraction procedure is shown in **Figure 2**. In **Table 2**, a summary of the stepwise sequential extraction procedure with pH solution values is shown, which involved a carbonate-bound fraction, an iron manganese-bound fraction and an organic-bound fraction [36–39].

Parameters	ICP-MS	AdDPCSV	Ref.
Detection limit	ng L^{-1}	pg L^{-1}	[29–30]
Sample mineralization	Yes	Yes	[28]
Matrix modifier	Yes	No	[28]
Interferences	High	Very few	[31]
Sample volume required	Very small	Very small	[30]
Ease to use	Moderate easy	Very easy	[30]
Method development	Difficult	Very easy	[30, 32]
Capital costs	Very high	Very low	[21, 28, 30]
Sensitivity	Very high	Extremely high	[21, 33]
Sample preparation	Destructive	Non-destructive	[33, 34]

Table 1. Comparison of elemental techniques for the analysis of PGMs.

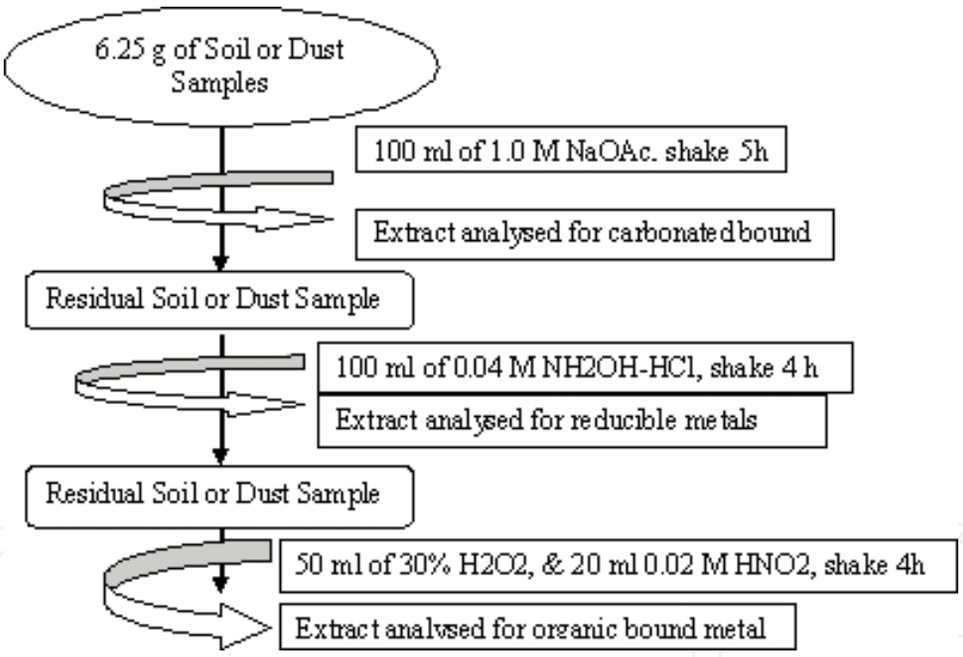


Figure 2. Sequential extraction procedure for trace metals in sediment, soil and dust samples.

Extraction fraction	Reactant concentration; pH
Carbonated bound	1.0 M NaOAc (sodium acetate); 2.0 pH = 4
Fe-Mn oxide bound	0.04 M NH_2OH–HCl (hydroxylamine hydrochloride), in 25% acetic acid; pH ≤ 2
Organic bound	A hydrogen peroxide (H_2O_2, 30%) solution including a 0.02-M HNO_3 solution; pH ≤ 2

Table 2. Summary and description of extracts used for each extraction step and the extraction phases of the sediments in the sequential extraction procedure [36].

Sample introduction			
Sample uptake rate		55 s	
Nebulizer type		Micromist	
Nebulizer gas		Argon, 0.9 L min^{-1}	
ICP-MS		**Data acquisition**	
RF power	1590 W	**Acquisition mode**	Peak hopping
Pulse stage voltage	15.70 V	**Stabilization time**	25 ms
Lens voltage	Omega Lens used	**Integration time**	0.5 s
Plasma gas	Argon, 0.98 L min^{-1}		
Auxiliary gas	Argon, 0.11 L min^{-1}		
Cones	Platinum		

Table 3. ICP-MS operating conditions for the determination of PGMs.

2.4.2. ICP-MS analysis

The analysis of the extracts produced by a sequential extraction procedure was achieved by using ICP-MS (Agilent Technologies, 7500 CX, Chemetrix, Midrand, RSA). Typical instrument operating conditions for the ICP-MS are listed in **Table 3**. The effects of plasma power, gas flow and sample depth were investigated in terms of PGM signal and interference formation. The standard solution of each of the metal ion was made in glass volumetric flask using double de-ionised water (18.2 mΩ cm) and the environmental samples were filtered through a 0.1 mm millipore filter. The concentration of the metals was then determined by means of extrapolation from a calibration plot.

2.4.3. Voltammetric analyses

Concentration of Pd, Pt and Rh in different speciation fractions were determined by adsorptive differential pulse cathodic stripping voltammetry (AdDPCSV). The instrument used was Epsilon analyser (BASi Instruments, West Lafayette, IN, USA) equipped with a three electrode system. The electrode set-up consisted of a conventional three electrode configuration, which comprised a glassy carbon (GC) working electrode, a Pt wire as counter electrode and silver/silver chloride (Ag/AgCl) as a reference electrode. Alumina micro polish and polishing pads (Buehler, IL, USA) were used for electrode polishing. A 0.2 M NaOAc buffer (pH = 5.2) solution was used as the supporting electrolyte. The volume of the voltammetric cell was 25 ml.

The sample containing each of the selected PGMs was conditioned by the addition of 0.2 M NaOAc buffer (pH = 5.2) solution and 1×10^{-5} M dimethylglyoxime (DMG) chelating reagent solution. Afterwards, 1 ml of sequentially extracted sample was placed into the voltammetric cell and the buffer was added. The solution was de-oxygenated for 150 s with high purity nitrogen and the adsorption study of PGMs was done using a pre-concentration potential of −1.2 V (vs. Ag/AgCl), under stirring conditions of 200 rpm for 120 s. The parameters measured in this technique are recorded in **Table 4**.

AdDPCSV	
Potential window	0.6–1.5 V
Electrodeposition potential	−1.2 V
Reduction time	120 s
Speed	200 rpm
Rest time	10 s
Time of deaeration with nitrogen	150 s

Table 4. Main parameters used in the adsorptive differential pulse cathodic stripping voltammetry.

Metal contents were determined by comparing voltammograms peak height from the sample with heights corresponding to standards on calibration graphs. The standard addition was used as a way of checking applicability of the calibration graph. All determinations were performed with five repetitions. From that series, basic statistical information was collected: mean values and standard deviations were calculated.

3. Results and discussion

3.1. Quality assurance

The analytical precision and quality assurance for the overall procedure was done by testing three sub-samples for each of the dust and soil samples. The AdDPCSV measurement showed good recoveries for all PGMs ions, with percentage recoveries between 89 and 112%. A blank sample consisting of an electrolyte (0.2 M sodium acetate buffer (pH = 5.2)) was used as a correction factor, the true concentration of the samples were taken as the difference between the measured concentrations of the samples to those of the blanks for each metal.

The procedural blanks were routinely analysed for every five samples. Since the certificate samples are not available, the analytical procedure was checked for accuracy by analysing enriched samples prepared by us. For metal contents lower than the detection limits a known quantity of Pd, Pt and Rh standards to samples of soil and dust was spiked [27]. The relative standard deviations on the metals measurements of recovery were found to be less than 15%.

3.2. Study of interferences

Precise and selective measurement of PGMs present in real sample matrices is a challenging task, as there are other commonly encountered cations and anions normally present in the real samples along with PGMs, posing a serious problem for electrochemical analysis. After obtaining the limits of detection, quantification and study of recovery, some possible interference in soil samples were investigated. Possible interfering ions of iron (Fe^{2+}), nickel (Ni^{2+}), cobalt (Co^{2+}), sodium (Na^{+}) and copper (Cu^{2+}) were tested using a 4:1 ratio of each metal ion possibly co-existing with selected PGMs. Interferences arising from oxygen containing

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inorganic ions of phosphate (PO_4^{3-}) and sulphate (SO_4^{2-}) that are expected to co-exist in PGMs were also evaluated [26, 40].

The results obtained have shown that although some of the cations appeared to have an interfering effect towards stripping analysis of PGMs complexes, the interfering was still at tolerable levels, as these ions only lead to approximately 5% decline in stripping peak current signals.

3.3. Analysis of soil samples by voltammetric and spectroscopic techniques

The concentration of the PGMs in soil samples was evaluated by AdDPCSV and ICP-MS analysis using the optimised parameters that are described in **Tables 1** and **2**, respectively.

As already mentioned in the introduction, concentration levels of PGM in environmental samples are very low, although a tendency to higher values is given due to anthropogenic impact. Analysis of the results in **Table 5** for sites OP1–OP4 and BOT1–BOT4 has been conducted to understand the prevalence of the PGMs at these sampling sites.

Table 5 shows mean concentrations and standard deviations for all the investigated sites. Analysis of the AdDPCSV and ICP-MS results that are shown in **Table 5** for Pd suggests that at OP sites, the major concentrations of Pd are associated with the Fe-Mn oxide-bound fraction, while at BOT sites, they are associated with the carbonated-bound fraction. The carbonated-bound fraction is considered to be introduced by land use activities (anthropogenic), which are considered to be weakly bound and, when in contact with the aqueous phase, will become more bio-available [41].

The Fe-Mn oxide-bound fraction has a scavenging effect and sometimes provides a sink of heavy metals, which can be unlocked under the correct redox potential and pH conditions [41]. The ICP-MS results obtained for Pt at the OP sites revealed that major concentrations are found in the Fe-Mn oxide-bound fraction. The BOT sites contained major concentrations of Pt in the carbonated-bound fraction. The results for the AdDPCSV analysis suggests that major concentration of Pt were found at the OP sites, while for the BOT sites the Pt concentrations were found in organic-bound fraction.

The ICP-MS results obtained for Rh at the OP sites revealed that the major concentrations were found in the Fe-Mn oxide-bound fraction, while for the BOT sites the Rh concentrations were obtained in carbonate-bound fraction.

Voltammetric results for Rh(III) analysis suggests that no major concentrations were found in extracted fractions of OP and BOT sampling sites. However, only for site BOT3 it was found that there were high concentrations of Rh in the organic-bound fraction. The results obtained for the samples collected at these sites detected by AdDPCSV analysis for Pd(II) ranged between 0.92 and 4.0 ng kg^{-1}. For Pt(II), the concentrations ranged between 0.84 and 0.99 ng kg^{-1}. For Rh(III), concentrations ranged between 0.42 and 1.21 ng kg^{-1}.

The results obtained for the samples collected at the OP and BOT sites, showed results for the ICP-MS analysis for Pd ranging between 0.01 and 0.34 μg kg^{-1}. For Pt the concentrations ranged between 0.004 and 0.07 μg kg^{-1}. For Rh, concentrations ranged between 0.002 and 0.26 μg kg^{-1}.

Soil samples							
Sites	**Fraction**	**AdDPCSV(ng g^{-1})**			**ICP-MS (μg g^{-1})**		
		Pd(II)	**Pt(II)**	**Rh(III)**	**Pd**	**Pt**	**Rh**
OP1	Carbonated	0.96 ± 0.01	0.93 ± 0.01	0.42 ± 0.01	0.02	0.01	0.005
	Fe-Mn	1.14 ± 0.05	0.94 ± 0.01	0.94 ± 0.01	0.198	0.01	0.01
	Organic	0.99 ± 0.01	0.92 ± 0.01	0.98 ± 0.01	0.01	0.004	0.002
OP2	Carbonated	0.98 ± 0.01	0.96 ± 0.04	0.92 ± 0.02	0.03	0.02	0.01
	Fe-Mn	1.17 ± 0.01	0.98 ± 0.01	0.94 ± 0.03	0.17	0.03	0.02
	Organic	0.97 ± 0.03	0.97 ± 0.02	0.96 ± 0.01	0.02	0.01	0.01
OP3	Carbonated	0.96 ± 0.02	0.96 ± 0.03	0.99 ± 0.01	0.04	0.01	0.02
	Fe-Mn	1.17 ± 0.01	0.84 ± 0.06	0.98 ± 0.01	0.15	0.04	0.03
	Organic	0.98 ± 0.01	0.97 ± 0.01	0.98 ± 0.04	0.03	0.03	0.02
OP4	Carbonated	0.98 ± 0.03	0.97 ± 0.01	0.98 ± 0.04	0.06	0.05	0.03
	Fe-Mn	1.17 ± 0.03	0.97 ± 0.01	0.97 ± 0.01	0.13	0.06	0.01
	Organic	0.99 ± 0.01	0.97 ± 0.01	0.97 ± 0.01	0.04	0.03	0.004
BOT1	Carbonated	1.04 ± 0.01	0.94 ± 0.01	0.86 ± 0.03	0.03	0.01	0.004
	Fe-Mn	0.98 ± 0.01	0.96 ± 0.01	0.96 ± 0.06	0.01	0.004	0.003
	Organic	0.94 ± 0.01	0.96 ± 0.01	0.76 ± 0.01	0.01	0.01	0.005
BOT2	Carbonated	1.31 ± 0.01	0.99 ± 0.04	0.99 ± 0.01	0.06	0.03	0.02
	Fe-Mn	0.98 ± 0.01	0.97 ± 0.01	0.98 ± 0.03	003	0.02	0.01
	Organic	0.94 ± 0.01	0.98 ± 0.01	0.75 ± 0.04	0.02	0.01	0.01
BOT3	Carbonated	4.00 ± 0.01	0.95 ± 0.01	0.95 ± 0.01	0.34	0.04	0.26
	Fe-Mn	0.98 ± 0.03	0.98 ± 0.01	0.97 ± 0.01	0.06	0.05	0.04
	Organic	0.97 ± 0.05	0.97 ± 0.03	1.21 ± 0.01	0.04	0.02	0.02
BOT4	Carbonated	0.92 ± 0.06	0.90 ± 0.01	0.86 ± 0.08	0.08	0.05	0.04
	Fe-Mn	0.98 ± 0.01	0.96 ± 0.02	0.86 ± 0.06	0.08	0.07	0.05
	Organic	0.98 ± 0.01	0.98 ± 0.01	0.75 ± 0.03	0.05	0.04	0.04

Table 5. Results obtained for the sequential extraction of PGM concentrations in soil samples obtained using AdDPCSV and ICP-MS analysis techniques.

Comparison of the above results has shown that better detection with AdDPCSV analysis was achieved, compared to the results obtained for ICP-MS analysis in **Table 5**.

Figure 3 displays the results obtained for the comparative analysis of PGMs by ICP-MS and AdDPCSV techniques in soil samples.

The results shown in **Figure 3** indicated that the results obtained for Pd seemed to be the highest at all of the investigated sampling sites, indicating that Pd(II) was the most mobile element in both spectroscopic and voltammetric results. The ICP-MS results showed the

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highest concentrations at site BOT3, followed by site OP1. AdDPCSV results showed the highest concentrations of Pd(II) at site BOT3, followed by site BOT2. Both the ICP-MS and AdDPCSV analysis were in agreement with the highest concentration of Pd found at site BOT3.

From the results shown in **Figure 3**, the order of abundance of PGMs in the soil samples was found to follow the order Pd > Pt > Rh. In this study, the concentration of Pd(II), Pt(II) and Rh(III) were successfully determined in the soil samples by AdDPCSV technique. The stripping peaks for Pd(II), Pt(II) and Rh(III) were obtained at average peak potentials of about

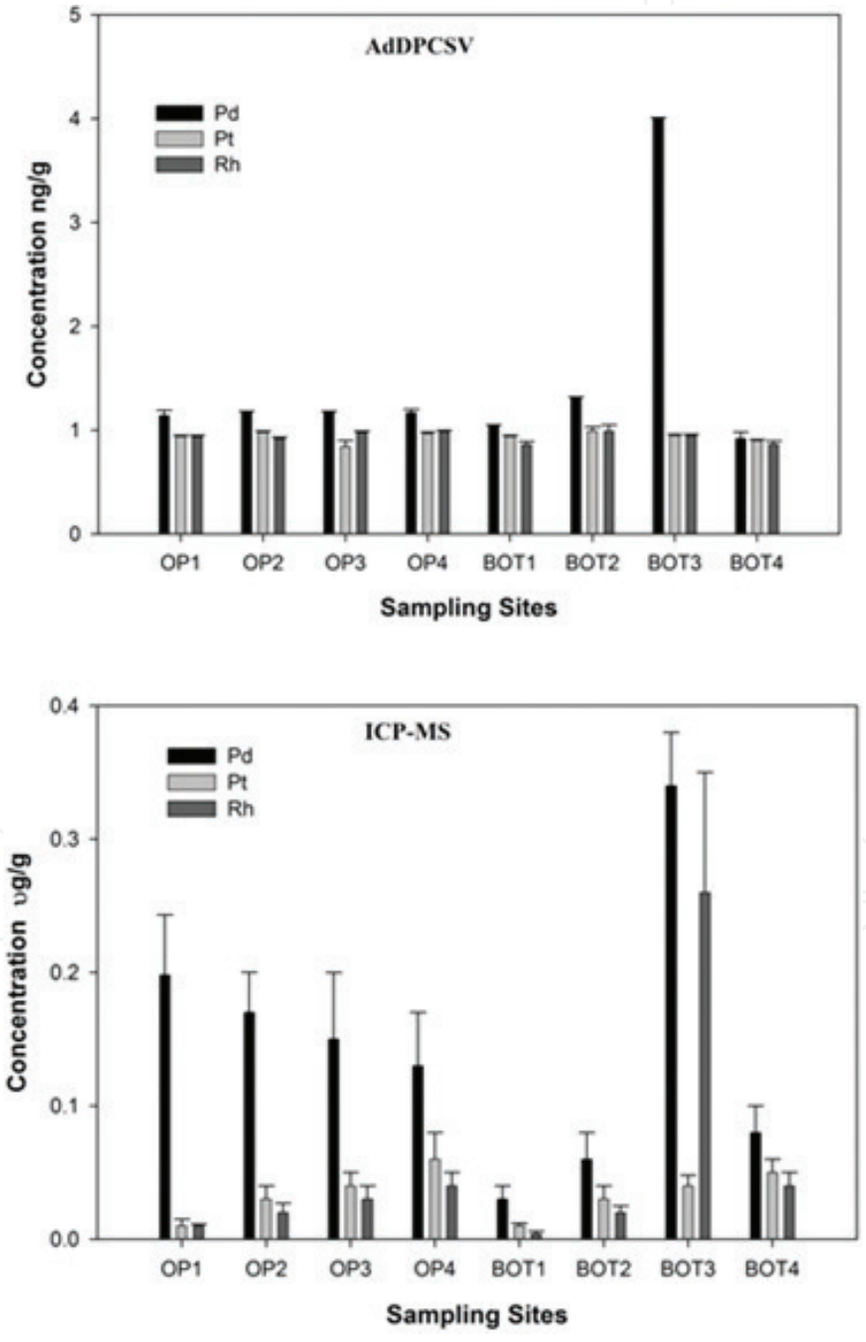


Figure 3. Comparative analysis of PGMs by ICP-MS and AdDPCSV techniques in soil samples.

−0.05, 0.04 and −0.25 V (vs. Ag/AgCl), respectively. These results showed a good comparison to the studies done by van der Horst et al. [26].

3.4. Analysis of dust samples by voltammetric and spectroscopic techniques

The PGMs levels in dust samples of the Bottelary (BOT) and Old Paarl (OP) Road samplings sites are outlined in **Table 6**. The experimental results for the AdDPCSV and ICP-MS analysis, displayed in **Table 4** revealed that for the OP sites, major concentrations of Pd was associated with the Fe-Mn oxide-bound fractions, while for the BOT sites it was associated with the carbonated-bound fractions.

The ICP-MS results obtained at sites OP4 and BOT4 revealed that major concentrations of Pt were found in the Fe-Mn oxide-bound fraction. The results obtained for the AdDPCSV analysis showed that major concentrations of Pt were found at sites OP2 and BOT2 in the carbonated-bound fraction.

The ICP-MS results obtained for Rh at the OP sites revealed no significant difference in concentrations obtained in the Fe-Mn oxide-bound and carbonated-bound fractions, while major concentrations at the BOT sites were obtained in the organic-bound fraction. The results for AdDPCSV analysis showed that no major concentration difference for the Rh concentrations were found in all of the fractions of all sites, except for site BOT3 that showed high Rh concentrations in the organic-bound fraction.

The results obtained for the samples collected at all sites detected by AdDPCSV analysis showed that the Pd(II) concentrations ranged between 0.96 and 1.35 ng kg^{-1}. The Pt(II) concentrations ranged between 0.87 and 0.99 ng kg^{-1}. The Rh(II) concentrations ranged between 0.10 and 0.95 ng kg^{-1}.

The results obtained for the samples collected at all sites detected by ICP-MS analysis showed that the Pd concentrations ranged between 0.02 and 0.15 μg kg^{-1}. The Pt concentrations ranged between 0.01 and 0.08 μg kg^{-1}. The Rh concentrations ranged between 0.002 and 0.26 μg kg^{-1}. These results obtained with AdDPCSV analysis showed better detection limits and were much lower values, compared to the results obtained for ICP-MS analysis (**Table 4**). It was therefore clear that the voltammetric technique was more sensitive than the spectroscopic technique investigated. Analysis of the results in **Figure 4** showed that the Pd concentrations were the highest at all of the investigated sites. It was again observed that Pd was the most mobile element in both spectroscopic and voltammetric results as observed in the results of **Figure 4**. The ICP-MS results showed the highest Pd concentrations at sites OP1 and OP3, followed by sites BOT3, OP4 and BOT2. Analysis of the AdDPCSV results showed the highest Pd concentrations at site BOT3, followed by site BOT4. The order of abundance of PGMs in the soil samples followed the order Pd > Pt > Rh.

3.5. Comparison between road soil and dust samples

Analysis of the PGMs concentrations was found to be generally a little bit higher in the soil samples than in the dust samples. A possible reason for this might be that the soil samples were taken from upper layer (0–2 cm), partly consisting of dust emitted from the roadway, containing particulate matter with PGMs.

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Dust samples							
Sites	**Fraction**	**AdDPCSV(ng g^{-1})**			**ICP-MS (μg g^{-1})**		
		Pd	**Pt**	**Rh**	**Pd**	**Pt**	**Rh**
OP1	Carbonated	0.99 ± 0.01	0.93 ± 0.01	0.40 ± 0.01	0.04	0.02	0.01
	Fe-Mn	0.99 ± 0.01	0.98 ± 0.01	0.15 ± 0.01	0.15	0.02	0.01
	Organic	1.05 ± 0.01	0.99 ± 0.01	0.93 ± 0.02	0.02	0.01	0.004
OP2	Carbonated	1.35 ± 0.01	0.93 ± 0.02	0.70 ± 0.01	0.07	0.04	0.03
	Fe-Mn	0.99 ± 0.01	0.97 ± 0.05	0.42 ± 0.06	0.06	0.04	0.03
	Organic	1.05 ± 0.01	0.95 ± 0.01	0.89 ± 0.01	0.03	0.02	0.01
OP3	Carbonated	1.35 ± 0.01	0.92 ± 0.01	0.70 ± 0.01	0.09	0.05	0.04
	Fe-Mn	0.99 ± 0.03	0.98 ± 0.01	0.25 ± 0.01	0.15	0.06	0.05
	Organic	1.00 ± 0.02	0.98 ± 0.01	0.95 ± 0.01	0.05	0.05	0.03
OP4	Carbonated	1.30 ± 0.01	0.96 ± 0.01	0.72 ± 0.03	0.06	0.06	0.05
	Fe-Mn	0.97 ± 0.03	0.96 ± 0.02	0.34 ± 0.03	0.13	0.09	0.06
	Organic	1.00 ± 0.02	0.96± 0.02	0.95 ± 0.04	0.04	0.06	0.03
BOT1	Carbonated	0.98 ± 0.01	0.93 ± 0.01	0.80 ± 0.01	0.03	0.06	0.005
	Fe-Mn	0.98 ± 0.01	0.87 ± 0.04	0.24 ± 0.02	0.01	0.02	0.01
	Organic	1.01 ± 0.01	0.99 ± 0.02	0.92 ± 0.01	0.01	0.02	0.01
BOT2	Carbonated	0.99 ± 0.01	0.99 ± 0.01	0.80 ± 0.01	0.06	0.08	0.03
	Fe-Mn	0.98 ± 0.02	0.89 ± 0.03	0.13 ± 0.05	003	0.04	0.02
	Organic	1.12 ± 0.01	0.99 ± 0.01	0.30 ± 0.02	0.02	0.05	0.03
BOT3	Carbonated	0.97 ± 0.01	0.92 ± 0.01	0.17 ± 0.01	0.34	0.09	0.04
	Fe-Mn	0.97 ± 0.01	0.94 ± 0.01	0.40 ± 0.01	0.06	0.08	0.04
	Organic	1.20 ± 0.01	0.95 ± 0.01	0.60 ± 0.01	0.04	0.06	0.04
BOT4	Carbonated	0.96 ± 0.02	0.89 ± 0.02	0.10 ± 0.08	0.08	0.10	0.05
	Fe-Mn	0.97 ± 0.01	0.91 ± 0.02	0.88 ± 0.06	0.08	0.09	0.07
	Organic	1.18 ± 0.01	0.96 ± 0.01	0.47 ± 0.01	0.05	0.08	0.05

Table 6. Results obtained for the sequential extraction of PGM concentrations in dust samples obtained using AdDPCSV and ICP-MS analysis techniques.

Although the AdDPCSV and ICP-MS techniques have different levels of detection, it was found that both soil and dust samples from all sampling sites have relatively high concentrations of Pd. Therefore, the observed Pd levels in soil and dust may either reflect the earlier introduction of Pd base catalysts or be indicative of the more widespread shift away from Pt towards Pd as the main catalytic component [42, 43].

The Pt: Pd ratios in environmental samples and the results of solubility experiments have suggested that Pd is more soluble than Pt or Rh and thus more susceptible to aqueous transport, resulting in its possible higher levels in the environment [44].

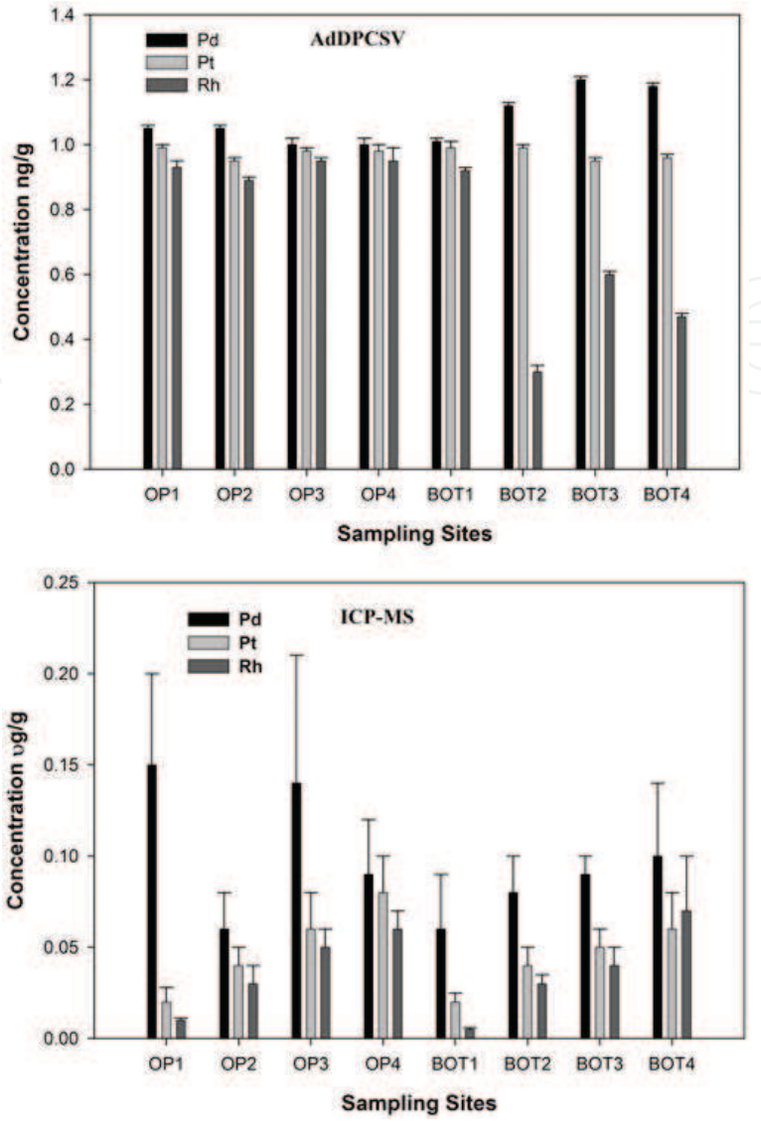


Figure 4. Comparative analysis of PGMs by ICP-MS and AdDPCSV techniques in dust samples.

The results obtained for the AdDPCSV and ICP-MS analysis in this study was also compared to the results obtained in other related studies. These results are displayed in **Tables 7–9**.

For comparison, the PGMs global concentration levels obtained using spectroscopic techniques are shown in **Table 7**. Analysis of the results in **Table 7** has shown that the past studies in South Africa investigated only platinum using ICP analysis in roadside dust samples. This study shows the concentration of all the investigated PGMs detected up to ng g^{-1}. Although this is an interesting result, it has no confirmation in the literature about Pd and Rh in South Africa. Both the global concentration and the results from the present study reveal that the introduction of catalytic converters to automobiles in the process of reducing the harmful emissions from the exhaust emissions has resulted in the increase of PGMs in roadside dust. This study is therefore updating the results for South Africa and comparing the results available for the international scenario.

The results in **Table 8** shows the levels of PGMs obtained in global roadside soil samples. Analysis of the results in **Table 8** has shown that most of the global studies have been done on ICP analysis for the detection of platinum in roadside soils. Both the global concentration

and the results from the present study reveal that the introduction of catalytic converter to automobiles in order to reduce the harmful emissions from car exhaust systems has resulted in the increase of PGMs in roadside dust matrices.

Roadside dust samples					
Country/city	**Pd**	**Pt**	**Rh**	**Unit**	**Reference**
South Africa/ Stellenbosch	20–150	10–80	4–74	ng g^{-1}	This study
South Africa/ Cape Town	–	4	–	ng g^{-1}	[25]
South Africa/Port Elizabeth	–	6	–	ng g^{-1}	[25]
South Africa/ Pretoria	–	23	–	ng g^{-1}	[25]
South Africa/ Rustenburg	–	223	–	ng g^{-1}	[25]
Ghana/Accra	–	39	–	ng g^{-1}	[45]
Germany/ Karlsruhe	–	112–169	–	ng g^{-1}	[44]
Germany/ Stuttgart	–	10	35	ng L^{-1}	[44]
Germany/ Frankfort	6	72	18	ng L^{-1}	[46]
Germany/ Frankfort	21.3	101.3	18.7	ng L^{-1}	[18]
Germany/ Unknown	1–146	5-8	–	ng g^{-1}	[47–49]
UK/Richmond	–	0.42–29.8	–	ng g^{-1}	[50]
UK/Nottingham	92.9	69.55	–	ng g^{-1}	[51]
Sweden/ Gothenburg	80	196	93	ng g^{-1}	[52, 53]
Sweden/ Unknown	213	56	74	ng g^{-1}	[47]
Poland/Bialystok	37.5	110.7	19.6	ng g^{-1}	[54]
Australia/Perth	37.5	110.7	19.6	ng g^{-1}	[55]
Austria/Styria	4	55	10.3	ng g^{-1}	[56]
Mexico/Mexico city	53.2–74	307.5–332.7	26–39.1	ng g^{-1}	[57]
Spain/Madrid	39–191	31–252	11–182.1	ng g^{-1}	[58]
Italy/Rome	102–504	14.4–62.2	1.9–11.1	ng g^{-1}	[59]
Greece/Ioannina	12.1–18.2	3.2–306	6.1–64.	ng g^{-1}	[60]

Table 7. Comparison of global concentration levels of PGMs in roadside dust samples by ICP spectroscopy analysis.

In **Table 9**, the results obtained for the voltammetric analysis of PGMs in roadside dust and soil samples are shown. Very few papers relevant to the voltammetric determination of PGMs in roadside soil and dust are reported in literature.

Roadside soil samples					
Country/City	**Pd**	**Pt**	**Rh**	**Units**	**Reference**
South Africa/ Stellenbosch	10–340	4–70	2–260	ng g^{-1}	This study
Ghana/Accra	–	15	–	ng g^{-1}	[45]
Germany/Hanau	–	23–112	–	ng g^{-1}	[18]
Germany/Mainz	7.2	87	–	ng g^{-1}	[61]
Germany/ Darmstadt	–	7.2–58.6	–	ng g^{-1}	[62]
Germany		15.6–31.7		ng g^{-1}	[63]
Germany		0.9–200		ng g^{-1}	[44]
Germany		27		ng g^{-1}	[64]
UK/Richmond		0.3–8		ng g^{-1}	[50]
UK/Nottingham		0.19–1.33		ng g^{-1}	[50]
UK/Birmingham		0.05–4.45		ng g^{-1}	[50]
Mexico city	307.5–332.7	53.2–74	26–39.1	ng g^{-1}	[58]

Table 8. Comparison of global concentration levels of PGMs in roadside soil samples by ICP spectroscopy analysis.

Country/city	**Pd**	**Pt**	**Rh**	**Units**	**Reference**
Roadside dust samples					
South Africa/ Stellenbosch	0.96–1.35	0.87–0.99	0.10–0.95	ng g^{-1}	This study
South Africa/ Stellenbosch	1.13–3.62	1.41–5.46	3.32–8.70	ng L^{-1}	[26]
Saudi Arabia/Jeddah city	192.3	–	–	μg L^{-1}	[65]
Roadside soil samples					
South Africa/ Stellenbosch	0.92–4.0	0.84–0.99	0.42–1.21	ng g^{-1}	This study
South Africa/ Stellenbosch	0.94–2.5	2.80–4.15	3.65–7.10	ng L^{-1}	[26]

Table 9. Comparison of global concentration levels of PGMs in roadside soil and road dust by voltammetric techniques.

http://dx.doi.org/10.5772/67699

Analysis of the results in **Table 9** has shown a lack of data in global concentrations of PGMs using voltammetric studies. One of the first investigations on roadside dust PGMs levels in Saudi Arabia was undertaken by Ba-Shami et al. [65]. This proves that voltammetric methods for detection of PGMs in road soil and dust samples are still in early stages globally. Most countries of the world have used spectroscopic studies to determine the concentration levels of PGMs in roadside dust and soil. The study by Ba-Shami et al. [65] has shown that voltammetric techniques can be applied to analyse roadside soil and dust samples for Pd(II) levels. In the current study, it was shown that voltammetric studies are sensitive enough to determine Pd(II), Pt(II) and Rh(II) in roadside soil and dust samples.

4. Conclusion

The present study showed the use of AdDPCSV analysis with a GCE/rGO-SbNPs sensor for the voltammetric determination of PGMs in roadside soil and dust samples. At all the sampling sites evidence of Pd, Pt and Rh were observed in different roadside media by AdDPCSV and ICP-MS analysis. The results showed that automobile catalysts are a minor source of PGMs into the South African environment with relatively low concentrations at high volume traffic sites near Stellenbosch, Western Cape. Useful analytical data on platinum group metal concentrations in soil and dust samples have been collected. Matrices effects in the samples were minimised by diluting the samples without the need of prior treatment for voltammetric analysis. The maximum concentrations of PGMs in road soil samples sampled near Stellenbosch using voltammetry were as follows: Pd(II) = 4 ng g^{-1}, Pt(II) = 0.99 ng g^{-1} and Rh(III) = 1.21 ng g^{-1}. The maximum concentration of PGMs in road soil samples near Stellenbosch using spectroscopy were as follows: Pd = 0.34 μg g^{-1}, Pt = 0.07 μg g^{-1} and Rh = 0.26 μg g^{-1}. The maximum concentrations of PGMs in roadside dust samples of Stellenbosch using voltammetry were as follows: Pd(II) = 1.35 ng g^{-1}, Pt(II) = 0.99 ng g^{-1} and Rh(III) = 0.95 ng g^{-1}. The maximum concentration of PGMs in roadside dust samples of Stellenbosch using spectroscopy were as follows: Pd = 0.34 μg g^{-1}, Pt = 0.10 μg g^{-1} and Rh = 0.06 μg g^{-1}. It was interesting to note that the data obtained in this study and compared to the globally available data revealed that Pt was the PGMs being investigated the most using spectroscopy as technique in the past. Unfortunately, not a lot of data are available concerning the voltammetric studies of PGMs in soil and dust samples. The lack of data in this field enables us to make only a few general comments. The improvement of LODs due to the development of novel analytical techniques has recently enabled detection of PGMs concentrations in the pg g^{-1} range. The results of our investigations showed voltammetry as more sensitive than spectroscopic methods. The research study confirmed the significant role of traffic-related activities as a source of particles of anthropogenic origin to urban road surfaces and surrounding environment. These particles contain heavy metals that may become available for transport with storm water runoff and eventually impact on receiving water quality and the aquatic ecosystem. The outcome of this study provides further evidence of the need for voltammetric methods for detection of PGMs pollution. Although environmental levels of PGMs are still relatively low, recent reports of a progressive increase in these concentrations makes further research essential.

Acknowledgements

The authors would like to thank the National Research Foundation (South Africa) and the CSIR (NRE, Stellenbosch) for supporting this research. We further acknowledge the support of the SensorLab, Chemistry Department, University of the Western Cape, Bellville, South Africa. A word of thanks also to the Chemistry Department, Faculty of Applied Sciences, Cape Peninsula University of Technology, Bellville, South Africa.

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