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Determination of traces of Pt and Rh in soil and quartz samples contaminated by automobile exhaust after an ion-exchange matrix separation

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ABSTRACT

Monitoring of PGEs content in the natural samples is a crucial point in the environment science since catalytic car converters have been introduced. In the presented paper application of a very sensitive voltammetric method for determination of traces of Pt and Rh in the environmental samples contaminated by automobile exhausts is discussed. Voltammetric measurements were carried out in the supporting electrolyte containing formaldehyde and semicarbazide. PGEs were separated from the digested solutions of soils or quartz samples, collected from monitoring plots—by applying an ion-exchange resin Cellex-T. Pt was very effectively separated from the matrix approaching nearly 100% recovery after its elution by hydrochloric acid. Moreover the conditions of soil and quartz samples digestion were discussed. To validate the obtained result an independent analytical method—ICP MS was applied and analysis of certified reference material road dust 723—was completed.

1. Introduction

The increasing interest in determination of platinum group elements (PGEs) in the environmental samples is a consequence of the introduction of autocatalytic converters in car engines (in the USA since 1975, in Europe since 1986) [1–4]. Catalytic converters are manufactured with ceramic or metal substrate, covered in an alumina washcoat containing metal additives like Zr or Ce. On the surface of the washcoat, varying proportions of PGEs—mainly Pt, Rh, and Pd—are highly dispersed. The particulate matter containing PGEs is emitted with the exhaust gas due to thermal and mechanical attrition during vehicle operation [5]. Pt, Pd and Rh are released into the environment. It is reported that emission from gasoline catalysts is expected to be in the low nanogram per km range, whereas 10–100-fold higher Pt emissions have been measured for diesel catalyst [6,7]. A global catalyst emission of 0.8–6.0 ton of Pt per year can be expected, assuming that 500 million vehicles are equipped with catalyst, that the average yearly mileage is 15,000 km per vehicle and that the average emission rate is 0.1–0.8 $\mu g\ km^{-1}$ [3]. In relation to the elevated PGEs content in the vicinity of roadways, a number of scientific works deal with the distribution and behavior of PGEs in roadside soils [8], road dust [8] or some plants—mainly grass [8,9]. As the concentration of these metals in the environment still remains at a very low level their analysis requires analytical methods of high sensitivity.

Stripping voltammetry as a technique has proven to be very useful in the analysis of metal ions [9–14]. It has excellent detection limits especially in case of Pt and Rh determination. The procedure is based on the potential supported accumulation of a platinum complex at the surface of a hanging mercury drop electrode. The electrochemically active complex lowers the hydrogen overpotential at the mercury electrode and thus produces a very sensitive catalytic current, which is measured in the differential pulse mode. For Pt determination supporting electrolytes containing formaldehyde and hydrazine [9,13,14], hydroxyloamine [10], acetone oxime [10], thiosemicarbazide [11], semicarbazide [12] can be found in the literature. In the presented work semicarbazide was chosen as a component of supporting electrolyte giving the possibility of simultaneous determination of Pt and Rh.

In environmental samples, the low concentration of platinum group elements together with the high concentration of interfering matrix components often requires an enrichment step combined with a matrix separation [15–17]. Most frequently for this purpose solid phase extraction methods are used [18]. The ion-exchange methods utilize a strong affinity of Pt chlorocomplexes

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for anion exchange resins and their low affinity for the cation exchangers [19].

2. Experimental

2.1. Instrumentation

For voltammetric measurements a μAUTOLAB electrochemical analyzer (The Netherlands) was utilized. A three-electrode arrangement was used, comprising a hanging mercury drop electrode (HMDE) as a working electrode, a saturated Ag/AgCl reference electrode, and an auxiliary glassy carbon electrode. Determinations were carried out in quartz voltammetric vessels. Other equipment used included: an Elan 6100 DRC inductively coupled plasma mass spectrometer SCIEX (PerkinElmer, USA) with a Meinhard nebulizer and cyclonic spray chamber; an ETHOS 1600 microwave digestion system (Milestone, Italy); a laboratory mill (Fritsch, Germany).

The following acids were used: HNO_3 ($d=1.40\ g\ mL^{-1}$), HCl ($d=1.15\ g\ mL^{-1}$), H_2SO_4 ($d=1.84\ g\ mL^{-1}$), and $HClO_4$ ($d=1.67\ g\ mL^{-1}$), Suprapur (Merck). 1 mg mL^{-1} standard solutions of Pt and Rh (Merck), formaldehyde (POCh Gliwice, Poland) and semicarbazide (Merck) were used. Thiourea (Sigma) was applied for SPE experiments. All solutions were prepared using deionized water obtained from a Milli-Q Water System, Millipore (USA).

2.2. Sampling and sample preparations

During undertaken investigation two kinds of samples were analyzed namely soil and quartz sand. The other was chosen as a natural matrix for the accumulation of traffic pollution over defined period of time. A layer of 157 cm of topsoil or ground cover (very close to the road it is usually not a natural soil) was removed and replaced with a plastic box (24 × 16 × 4 cm) containing clean quartz sand of known chemical composition and neutral magnetic properties (diamagnetic). The applied quartz sand (commercially available, with pure quartz content above 95% and granularity 0–1 mm) was initially washed in deionized water and dried. Quartz sand samples were collected for analysis after 6 months of exposition to automobile exhausts. About 1 kg of soil from two monitoring plots and 0.5 kg of quartz sand collected from the top layer (0–2 cm) were placed in plastic bags and transported to the laboratory. Then the samples were air dried and sieved through 1 mm sieve. Before the analysis the samples were additionally crumbled in a ceramic mortar.

2.3. Microwave decomposition

2.3.1. Decomposition of road dust BCR 723 material

Decomposition of BCR 723 material was performed after procedure optimization. 200 mg of BCR material and mixture of acids 3 mL HNO_3 and 4 mL HCl were placed in PTFE vessels and digested in a microwave digestion system. A three-stage program with a maximum temperature of 200 °C and a maximum microwave power of 1000 W was used (5 min: 20–90 °C; 10 min: 90–170 °C; 50 min: 170–200 °C). In the next step solutions were either evaporated or directly diluted with deionized water and PGEs were determined using the ICP MS technique.

2.3.2. Decomposition of soils and sands samples

Approximately 200 mg of homogeneous, dried soil sample or quartz sand sample and a mixture of concentrated acids (3 mL of HNO_3 and 4 mL HCl or *aqua regia*) were placed in PTFE vessels and digested in a microwave digestion system. A three-stage program with a maximum temperature of 200 °C and a maximum microwave power of 1000 W was applied. All samples were processed in triplicate. Digested samples were either evaporated or directly diluted with deionized water and PGEs were determined using ICP MS. In case of voltammetric determinations solutions after evaporation were diluted with 0.1 mol L^{-1} HCl.

2.4. Determination of the elements

ICP MS was used for determination of Pt and Rh (measured isotopes: ^{194}Pt, ^{195}Pt, ^{196}Pt, and ^{103}Rh)—under conditions described before [8]. Voltammetric determinations were conducted according to the following published papers: Pt and Rh were determined using the AdSV method in a supporting electrolyte containing H_2SO_4, HCHO and semicarbazide (HCl) [12].

2.5. Solid phase extraction procedure

Polyethylene syringes were packed with 200 mg or 400 mg of Cellex-T sorbent and both ends of tube were blocked with polyethylene frits. Through freshly prepared column 5 mL of 2 mol L^{-1} HCl solution and 15 mL of Milli-Q water were passed. Then 5 or 10 mL of sample solution in 0.1 mol L^{-1} HCl was passed through the column. After that to dilute the interfering ions 2 mL of 0.1 mol L^{-1} HNO_3 was applied. Finally the retained analytes were eluted by 2–10 mL of 2 mol L^{-1} HCl solution or 4 mL of 0.1 mol L^{-1} thiourea in 0.1 mol L^{-1} HCl. Columns were regenerated before next usage by application of 2 mol L^{-1} HCl.

3. Result and discussion

In the first stage of studies experiments were focused on optimization of digestion procedures and preconcentration of PGEs using solid phase extraction as main steps in analysis of the environmental samples in which traces of Pt and Rh have to be determined. A lot of attention was paid to the reliability of the obtained results; therefore our research was started with a comparison of various procedures used for the digestion. Due to the fact that neither soil nor quartz sand certified reference materials are available, road dust BCR 723 was chosen for the analysis. An optimized digestion procedure was applied for soil and quartz sand samples and additionally the recovery study was done.

3.1. Optimization of the digestion procedure

According to the literature [8,13,16,20], for the decomposition of solid samples such as soils and minerals different mixtures of HNO_3 and HCl with or without HF are recommended and widely used. Therefore in our studies we checked and compared a number of different mixtures consisting of these acids to choose the most appropriate one.

3.1.1. Optimization of the digestion procedure of certified material—road dust—BCR 723

In the first step 200 mg of BCR 723 was weighed into crucibles and 3 mL of *aqua regia* was added. Crucibles were placed on a hotplate. After digestion and cooling, 0.5 mL of HF was added and the digestion was continued. After approximately 2 h, 1 mL of H_2SO_4 was added and digestion was continued for another 2 h. Digestion was carried out at approximately 150 °C.

In the second step of investigation 250 mg of road dust was weighed into Teflon vessel and the following mixtures of acids were added: (a) 2.25 mL HCl + 0.75 mL HNO_3; (b) 2.25 mL HCl + 0.75 mL HNO_3 + 0.5 mL HF; (c) 3 mL HNO_3 + 4 mL HCl; (d) 3 mL HNO_3 + 0.5 mL HF; (e) 2 mL HNO_3 + 1 mL $HClO_4$; (f) 2 mL HNO_3 + 1 mL $HClO_4$ + 0.5 mL HF. The following digestion program with maximum microwave power of 1000 W was applied: 0–5 min/90 °C, 5–10 min/170 °C, and 10–50 min/200 °C. Digested samples were quantitatively transferred into polyethylene vessels and diluted by weight to 10 g. Next, either 4 mL of the sample was evaporated almost to dryness or the whole sample was filtered and evaporated. Evaporated samples were diluted with water before determination.

In addition, a two-step microwave accelerated digestion in a closed system was investigated. 250 mg of road dust was weighed into Teflon vessel and the following mixtures of acids were added: (a) 2.25 mL HCl+0.75 mL HNO_3; (b) 3 mL HNO_3; (c) 2 mL HNO_3+1 mL $HClO_4$. Digestion was performed using the digestion program given above. 0.5 mL of HF was added after cooling of Teflon vessels and the digestion procedure was continued. At this stage of the experiment all analysis were carried out using the ICP MS technique. Results of determination of platinum and rhodium are presented in Table 1. The results obtained for platinum and rhodium in BCR 723 pointed out that the mixture of hydrochloric acid and nitric acid (4:3) is optimal. This digestion method, which was applied in further studies, is relatively short and does not require the addition of HF. The other acid mixtures and procedures did not provide suitable results.

3.1.2. *Optimization of the digestion procedure for soil and quartz sand samples*

Based on the results obtained for certified reference material, during studies related to samples of soil and quartz sand digestion with the usage of *aqua regia* and the mixture of nitric acid and hydrochloric acid in the ratio of 4:3 was examined. The comparison was carried out for two selected soil samples and two quartz sand samples. Microwave accelerated digestion was carried out according to the procedure developed for road dust. 250 mg of the sample was weighed into Teflon vessel and one of the acid mixtures was added: (a) 3 mL HNO_3+4 mL HCl; (b) 2.25 mL HCl+0.75 mL HNO_3. Further steps were consistent with the procedure described for road dust samples. Results of determination of Pt and Rh in soil samples are presented in Table 2.

Based on the obtained results it could be concluded that both of the mixtures: nitric acid and hydrochloric acid in the ration of 4:3 and *aqua regia* give comparable results and can be applied during digestion of soil samples (Table 2). To assess the results of mineralization with different acid mixtures, a *t*-test (two-tailed, $P=95\%$) was conducted on the mean values. The results did not differ significantly ($t_{exp} < t_{crit}$; Table 2). The digestion results obtained using two different acid mixtures were not significantly different.

Similar results were obtained for quartz sand. The same mixtures of nitric and hydrochloric acids were applied. Due to the low content of the analyzed elements recoveries from enriched samples were tested (addition of 20 ng Pt and Rh was applied). The recovery of Pt and Rh was close to 100% (3 mL HNO3+4 mL HCl→98 ± 4%, aqua regia→112 ± 4%, $t_{exp}=4.24$, and $t_{cryt}=4.30$).

As both digestion methods give comparable results, in further studies we used the mixture of HNO_3 and HCl in the ratio 1:3. That ensured the reduction of the amount of applied acids and as a consequence a shorter time of the evaporation of the samples after the digestion step [8,19].

3.1.3. *Recovery studies*

To prove reliability of the proposed digestion procedure additionally the recovery studies were done. 250 mg of the soil sample was spiked with: Pt standard solution (250 ng of Pt); Rh standard solution (250 ng Rh), separately or as a mixture and 2.25 mL HCl+0.75 mL HNO_3 was added. Digestion was performed using the digestion program given above. In the next step solutions were either evaporated or directly diluted with deionized water and PGEs were determined. Recovery for Pt and Rh is close to 100% in both procedures—with and without evaporation step.

3.2. *Optimization of the solid phase extraction procedure*

Because of the low concentration of PGEs in the environment very often it is necessary to preconcentrate them and separate from other species before determination [19]. Therefore solid phase extraction was tested for Pt and Rh. As a method of detection in undertaken studies ICP MS was used and in case of PGEs analysis additionally adsorptive stripping voltammetry was applied.

After preparation of SPE column—according to the procedure described in the Section 2.5—5 or 10 mL of a model solution containing platinum and rhodium was passed through self-made SPE column containing anion-exchange Cellex-T sorbent. In the collected eluats PGEs were determined. It was found that rhodium did not adsorb on the column—almost 90% was passed through. The content of Pt in the eluats did not exceed 5%.

In the next step the attention was focused on the efficient elution of Pt from the SPE column. For that purpose mainly thiourea solution is recommended [16,19]. Based on our studies it could be stated that regardless of the pH of thiourea solution, the recovery of platinum does not exceed 75%. In addition, the presence of thiourea, as an organic solution, strongly influences

Table 2
Results of determination of Pt and Rh in two soil samples by ICP MS after digestion with a mixture of HNO_3 and HCl in different ratios ($n=4$); C ± SD.

	Sample	HNO_3:HCl 3:4 ($ng\ g^{-1}$)	HCl:HNO_3 3:1 ($ng\ g^{-1}$)	F_{eks}	t_{exp}	F_{kryt}/t_{kryt}
Rh	Soil A	33 ± 3	35 ± 1	10.89	0.76	15.44/2.447
	Soil B	11 ± 3	14 ± 3	1.00	0.93	
Pt	Soil A	95 ± 7	88 ± 6	0.79	1.02	
	Soil B	32 ± 2	32 ± 1	0.16	0.09	

Table 1
Results of determination of Pt and Rh in BCR 723 digested using different acid mixtures and digestion procedures C ± SD.

Digestion system	Reagents	*n*	Pt ($ng\ g^{-1}$)	Rh ($ng\ g^{-1}$)
Open	1st step: 3 mL of aqua regia; 2nd step: 0.5 mL HF; 3rd step: 1 mL H_2SO_4	3	23 ± 5	< 5
Closed	2.25 mL HCl+0.75 mL HNO_3 evaporation	3	45 ± 1	< 5
Closed	2.25 mL HCl+0.75 mL HNO_3+0.5 mL HF evaporation	3	20 ± 1	< 5
Closed	3 mL HNO_3+4 mL HCl evaporation	4	80 ± 3	13 ± 1
Closed	3 mL HNO_3+0.5 mL HF evaporation	3	16 ± 2	< 5
Closed	2 mL HNO_3+1 mL $HClO_4$ evaporation	3	24 ± 2	< 5
Closed	2 mL HNO_3+1 mL $HClO_4$+0.5 mL HF evaporation	3	34 ± 2	< 5
Closed	1st step: 2.25 mL HCl+0.75 mL HNO_3; 2nd step: 0.5 mL HF evaporation	3	16 ± 1	< 5
Closed	1st step: 2 mL HNO_3+1 mL $HClO_4$; 2nd step: 0.5 mL HF evaporation	3	24 ± 1	< 5
Closed	1st step: 3 mL HNO_3; 2nd step: 0.5 mL HF evaporation	3	8 ± 1	< 5
Closed	1st step: 3 mL HNO_3 evaporation; 2nd step: 2.25 mL HCl+0.75 mL HNO_3 evaporation	3	28 ± 3	< 5
Certified value BCR 723			**81.3 ± 2.5**	**12.8 ± 1.3**

voltammetric determination of PGEs. Moreover, it was stated by Pyrzyńska [18] that sorbent that has been in contact with thiourea solutions has a lower capacity for platinum complexes. Considering the abovementioned factors the solution of thiourea was replaced with 2 mol L^{-1} hydrochloric acid. In order to optimize the volume of the eluent, the elution was carried out with 2, 3, 4, 5, or 10 mL of a 2.0 mol L^{-1} HCl. The volume of the eluent, required to complete the elution of retained platinum, was matched as 5.0 mL or more. Change of the eluent allowed to get nearly 100% Pt recovery (in respect to 36.7 ± 4.2% obtained with 4 ml HCl reported by Leśniewska et al. [19]).

To find optimal mass of sorbent columns were packed with 100 mg, 200 mg and 400 mg of Cellex-T. The whole procedure was continued as described above. The most replicable results were obtained using columns with 400 mg of resin.

Then, maximum volume of applicable sample solution was checked. It was found that even 50 mL of sample solution gave good recoveries and allowed to preconcentrate the analytes 10-fold. During the experiment the possibility of multiple use of prepared SPE columns was tested. Fairly repeatable results of platinum and palladium recoveries were obtained.

Finally, the recovery of PGEs from ion exchanged resin from the standard solutions containing besides Pt and Rh other metal ions like Pb, Cd, Ni, Zn, and Fe was tested. The sample was applied to the sorbent in hydrochloric acid medium, which ensured the formation of chloride complexes of PGEs. A study found that introduced elements, with the exception of Pt, in more than 85% passed through the sorbent (Fig. 1). The remaining 10% was washed with nitric acid in a stage before elution of the analytes.

Based on the obtained results, it can be stated that the optimized extraction procedure with the use of sorbent Cellex-T may be applied prior to the determination of platinum in the samples containing various metal ions, such as soils and quartz sands associated with road transport.

3.3. Voltammetric determination of platinum

For the determination of platinum in the environmental samples such as soils and quartz sand exposed to pollution connected with high traffic, the procedure with semicarbazide, described in our previous work [12], was applied.

First, voltammograms for Pt standard solutions passed by SPE column were recorded. The recovery of platinum in the solution of 2 mol L^{-1} HCl applied as an eluat was 100 ± 1%. Moreover, no influence of the solution component on voltammograms‘ shape was observed (Fig. 2).

To verify the applicability of the analytical procedure the method was applied to standard reference material BCR 723

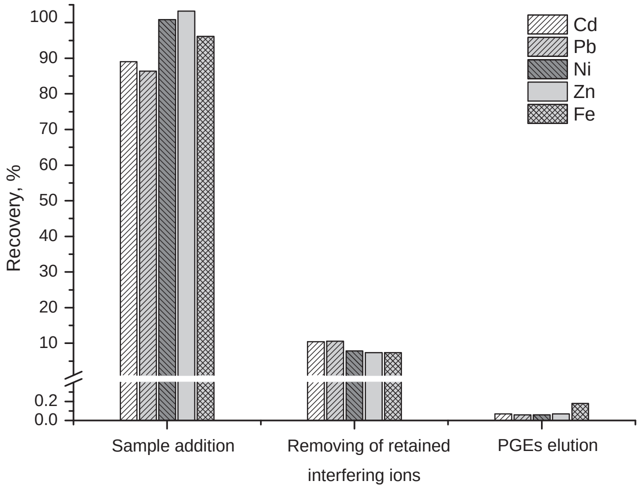

Fig. 1. Recovery (%) of elements in effluents collected after each stage of the matrix separation procedure.

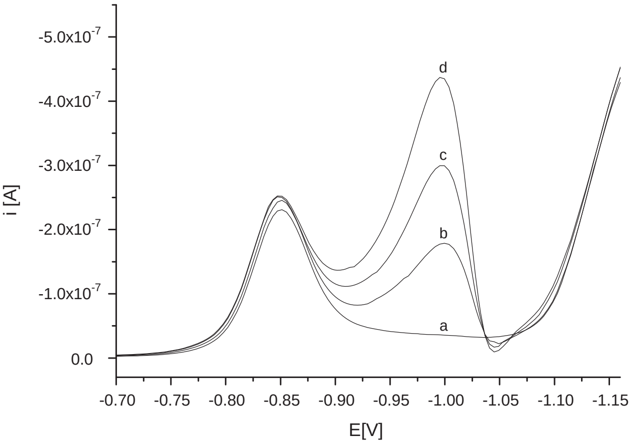

Fig. 2. Adsorptive stripping voltammograms of supporting electrolyte containing 0.24 mol L^{-1} H_2SO_4, 0.010 mol L^{-1} HCHO, 0.15 mmol L^{-1} semicarbazide (a), eluate of standard solution (b) and additions of 3.3 ng L^{-1} (c) and 6.6 ng L^{-1} (d) of platinum.

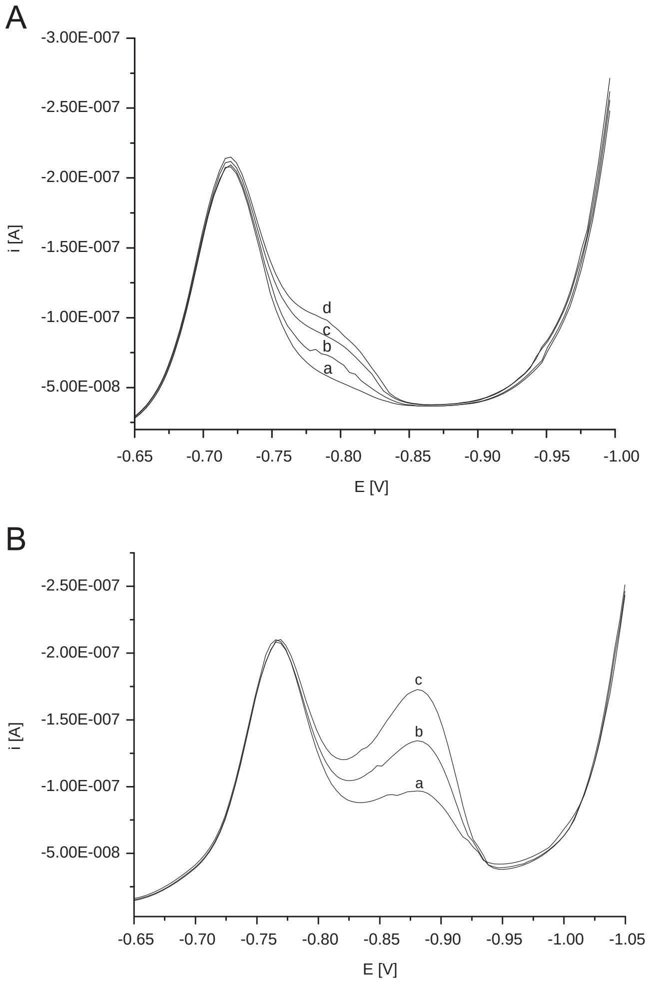

Fig. 3. Adsorptive stripping voltammograms of (A) mineralized BCR 723 material in supporting electrolyte containing 0.24 mol L^{-1} H_2SO_4, 0.010 mol L^{-1} HCHO, 0.15 mmol L^{-1} semicarbazide (a) and additions of 6.6 ng L^{-1} (b), 13.2 ng L^{-1} (c) and 20 ng L^{-1} (d) of platinum (B) eluate of BCR 723 material (a) and additions of 6.6 ng L^{-1} (b) and 13.2 ng L^{-1} (c) of platinum.

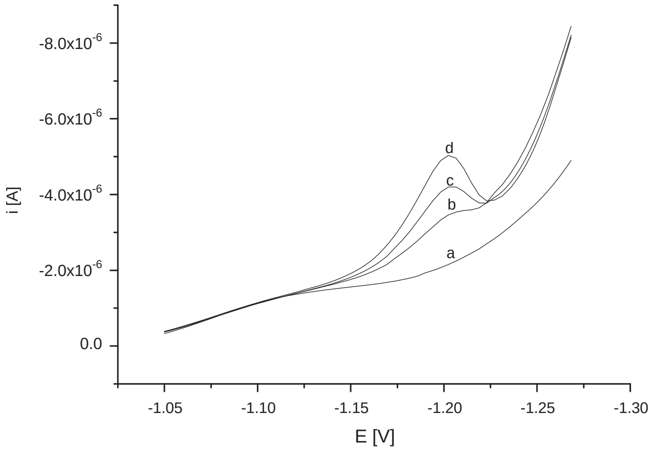

Fig. 4. Adsorptive stripping voltammograms of supporting electrolyte containing 0.24 mol L^{-1} H_2SO_4, 0.010 mol L^{-1} HCHO, 0.15 mmol L^{-1} semicarbazide (a), mineralized soil sample (b) and additions of 6.6 ng L^{-1} (c) and 13.2 ng L^{-1} (d) of rhodium.

Table 3
Comparison of the results of rhodium and platinum contents in soil and enriched quartz sand (20 ng–1 g) samples digested with a mixture of HNO_3:HCl (1:3) and separated on SPE column ($n \geq 2$); C ± SD.

	Sample	AdSV (ng g^{-1})	ICP MS (ng g^{-1})	t_{exp}	t_{kryt}
Rh	Quartz sand	$21 \pm 1 [n=4]$	$21 \pm 1 [n=2]$	1.14	2.77
	Soil C	$47 \pm 11 [n=16]$	$41 \pm 5 [n=9]$	1.89	2.07
Pt	Quartz sand	$24 \pm 1 [n=6]$	$22 \pm 1 [n=3]$	2.00	2.36
	Soil C	$263 \pm 22 [n=6]$	$245 \pm 18 [n=8]$	1.63	2.18

(road dust). The ability to determine platinum before and after solid phase extraction was compared (Fig. 3). Only after SPE, values (82 ± 3 ng g^{-1}) corresponding with certificate (81.3 ± 2.5 ng g^{-1}) were obtained.

In the next step platinum was electrochemically determined in quartz sand samples. Due to very low Pt content the investigated samples were enriched by the addition of 20 ng of Pt standard solution. The digestion was carried out according to the previously described procedure. Electrochemical determinations of Pt were performed in the samples without or after SPE (Fig. 4). In both cases obtained results 25 ± 5 ng g^{-1}and 24 ± 1 ng g^{-1}, respectively, were in good agreement with the results obtained by ICP MS (23 ± 1 ng g^{-1}) although the results obtained in the solutions after SPE were characterized by considerably greater reproducibility. To assess the quality of the results obtained by spectrometric and voltammetric techniques, a *t*-test (two-tailed, $P = 95\%$) was conducted on the mean values. Both sets of results did not differ significantly ($t_{exp} < t_{crit}$). The results obtained from spectrometric and voltammetric measurements were not significantly different [$t_{exp} = 1.97 < t_{crit} = 2.26$].

3.4. Voltammetric determination of rhodium

In case of Rh the influence of sample matrix on electrochemical determination and shape of analytical signal was negligible (Fig. 4). So the AdSV determinations of this element were carried out in aliquots of digested solutions after evaporation near to dryness and dilution to 5 mL by deionized water. The obtained results were presented in Table 3. The electrochemical results were compared with the result obtained by ICP MS.

4. Summary

The presented investigation illustrated the usefulness of the adsorptive voltammetry method in the examination of PGEs content in the environmental samples collected in the vicinity of roads. The strong influence of matrix component was discussed and the applicability of SPE before electrochemical determination was proven. Obtained results were validated by analysis of CRM road dust, recovery study and measurements by two independent analytical methods—AdSV and ICP MS.

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