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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.

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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 $\mu\text{g km}^{-1}$ [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 μ AUTOLAB 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 ($d=1.40 \text{ g mL}^{-1}$), HCl ($d=1.15 \text{ g mL}^{-1}$), H_2SO_4 ($d=1.84 \text{ g mL}^{-1}$), and HClO_4 ($d=1.67 \text{ g mL}^{-1}$), 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 ($24 \times 16 \times 4 \text{ cm}$) 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: $20\text{--}90^\circ\text{C}$; 10 min: $90\text{--}170^\circ\text{C}$; 50 min: $170\text{--}200^\circ\text{C}$). 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 ,

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