Polish J. of Environ. Stud. Vol. 16, No. 3 (2007), 329-345

Review

Platinum Group Elements: A Challenge for Environmental Analytics

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Received: May 29, 2006
Accepted: January 4, 2007

Abstract

An increased worldwide usage of platinum group elements *(PGE)* has been observed during recent decades. High amounts of *PGE* are applied in such areas as chemical industry and jewellery production, but the increased demand for these metals primarily depends on the introduction of automobile catalytic converter systems. Catalytic converters have also been considered to be a major source of PGE pollution. The similar Pt:Rh ratio, which is used in these autocatalysts, was found in various environmental samples as well. The present literature review indicates that the concentration of these metals has increased considerably in the last twenty years in different environmental matrices, resulting in ecological and human health risks. Because of the importance of *PGE* and their trace levels in environmental and biological matrices, sensitive methods are required for reliable determination. Details of the particular steps of analytical procedures for *PGE* quantification in environmental samples such as road dust, airborne particulate matter, soil, benthic sediments, water, wastewater and biological samples are discussed. Sampling and sample storage and preservation techniques are presented. Moreover, the most frequently used extraction, enrichment, detection and determination procedures for *PGE* are described.

Keywords*:* platinum group elements, autocatalyst, urban environment, environmental samples, sampling, sample pretreatment and storage, extraction and enrichment of analytes, determination methods, *ICP-MS*.

Introduction

Platinum group elements (PGE) include metals such as platinum (Pt), palladium (Pd), rhodium (Rh), ruthenium (Ru), iridium (Ir) and osmium (Os). These elements are present in environmental samples (*e.g.* soil, road dust, airborne particulate matter, water, benthic sediments and biota) at very low concentrations. However, due to the intensified development in specific sectors of human activities an increasing trend in those concentrations has been observed. The main emission source of *PGE* into the environment, except for the emissions of geogenic and cosmic origin, are human activities [1].

By far the greatest usage of *PGMs (platinum group metals)* both in Europe and worldwide is in vehicle catalysts, with additional major applications in the chemical industry, electrical and electronics industries, petroleum industry, the manufacture of jewellery, as a cancer-treating drug in medicine, as alloys in dentistry and in the glass industry. The data on the consumption of PGEs are shown in Fig. 1.

Automobile catalysts are both major and mobile source of *PGEs*. Due to the wear of catalytic converters in motor vehicles such elements as Pt, Pd and Rh bound to the carrier molecules penetrate into the environment [3] (see Fig. 2). Depending on the operating conditions and

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the age of the converter, mean platinum emissions range from 7 to 123 ng m^{-3}, corresponding to emission factors between 9 and 124 ng km $^{-1}$ [4].

Hospital effluents containing Pt drugs also are an important source for the emission of Pt into wastewater and sewage sludge. It was reported that total platinum emissions into the public sewage systems via hospitals were approx. 14.3 kg of Pt in 1996 in Germany, which corresponds to approx. 187.2 kg of total Pt from cars [5].

The actual amount of *PGEs* released into the environment by catalysts can be directly evaluated by determining their content in car exhaust fumes or by quantifying the anthropogenic *PGE* in environmental materials such as soil, airborne particles, sludge, water, road dust, etc. and modeling these data together with traffic statistics. Table 1 shows the results obtained by authors following these two strategies.

Until recently, studies on background concentrations of platinum group elements in the environment were mainly based on the determinations of Pt levels, later to be followed with Pd and Rh concentration measurements. In the cases of Ir, Ru and Os, only very scarce data are available. This is mainly due to the fact that the available analytical techniques and methodologies are also limited. Determination of Ru and Os is particularly difficult because both elements form volatile oxides [14]. Thus this is the additional reason that explains the scarcity of data on the content of these elements in environmental samples.

Investigating *PGE* content in environmental samples poses a big challenge because of the following:

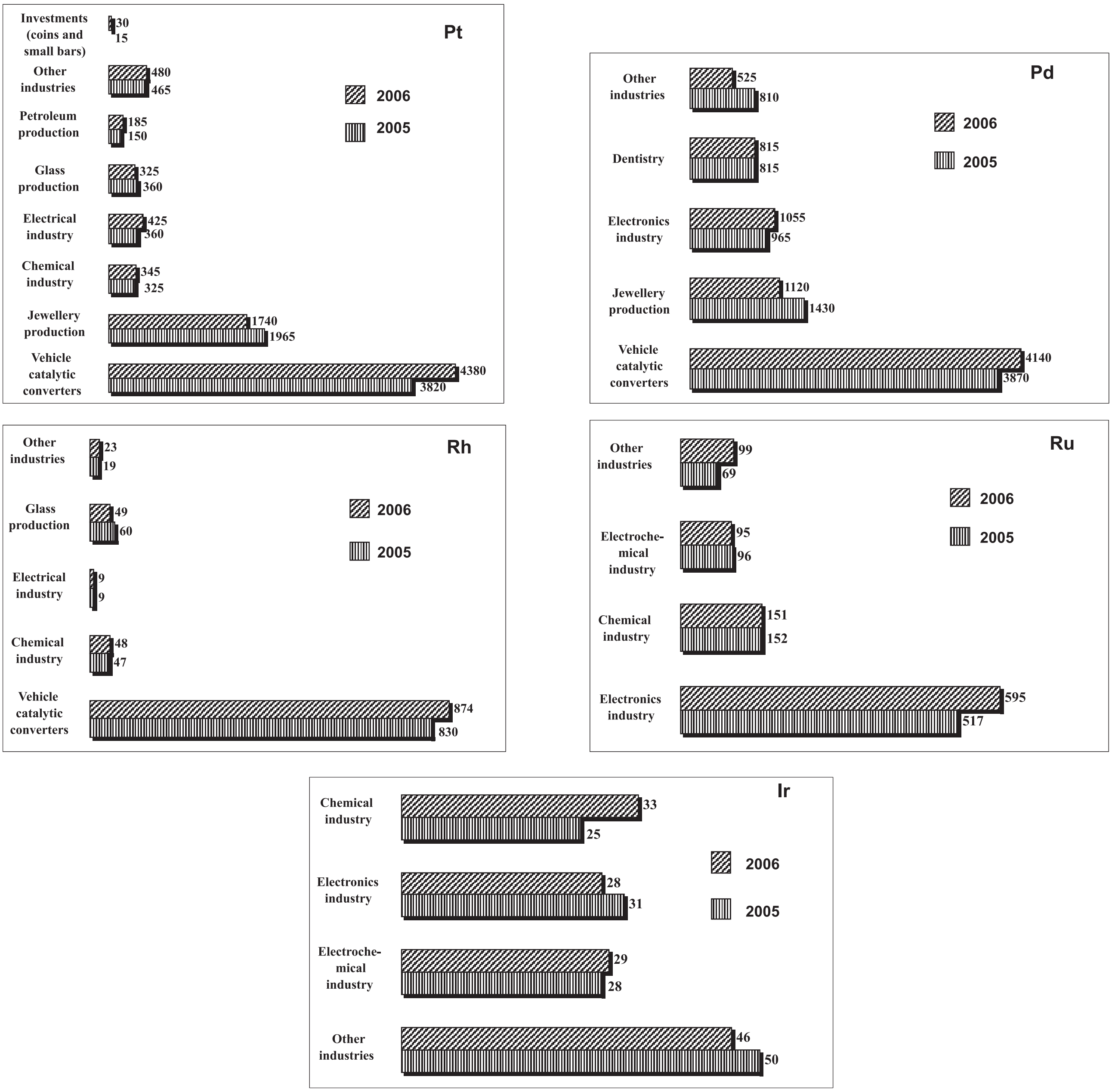

Fig. 1. World consumption of PGEs [10^3 oz] in 2005 and 2006 [2].

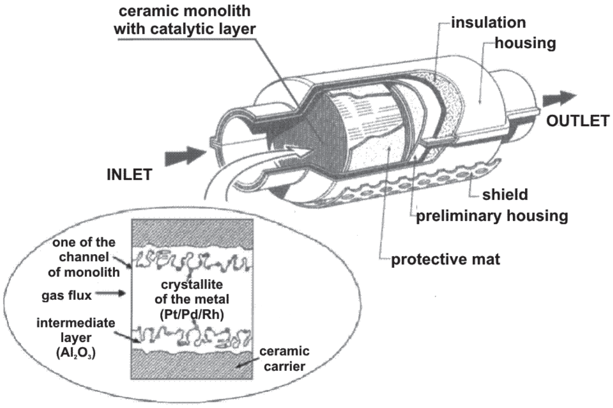

Fig. 2. Cross section of a typical vehicle exhaust catalyst, including the single channel of a monolith [6].

- very low concentration levels of analytes
- difficulties with quantitative dissolution of samples
- lack of proper reference materials
- unsatisfactory metrological characteristics of the analytical techniques used in the final determination step.

Because of the above-mentioned reasons it is necessary to introduce additional steps into the specific analytical procedures in order to obtain reliable analytical results of good quality.

Analytical Procedures for Platinum Group Elements Present in Environmental and Biological Samples

As mentioned before, the precise determination of low levels of *PGE* in environmental samples is possible only when instrumental techniques characterized by low limits of quantification (*LOQ)* are employed. Proper sampling and sample pretreatment techniques are a must if sample contamination or the loss of analytes is to be avoided. The following types of environmental samples analyzed for *PGE* content have been described in literature:

- road dust
- airborne particulate matter
- soil and benthic sediments
- water
- wastewater
- biological samples.

In further parts of this publication the literature data on basic problems experienced during dissolving, enriching and determining the *PGE* analytes in the above-mentioned types of samples have been presented.

Sampling, Storage and Preservation of Samples for Analysis

Road Dust

Road dust is becoming a significant factor in evaluating environmental conditions, particularly in metropolitan areas. Its main components are [15]:

- soil
- soot
- airborne particulate matter
- organic matter originating from local vegetation
- pollutants from road transport
- salt,
- gravel,
- debris from road accidents
- components of road pavement
- garbage and animal remains

Road dust samples could be collected by hand brushing with a nylon brush and plastic collection pan directly from the road surface. Each brush and pan should be considered disposable and used only once. The samples were collected using latex gloves and were stored/transported in plastic sample bags [16]. Dust can also be collected by means of commercially available vacuum samplers equipped with cellulose filters [17]. The size of a representative dust sample for the analysis of *PGE* content has to be precisely determined; usually, it depends on the particle size distribution of a given dust. In case of particles < 90 µm (after grinding), samples of about 0.1 g are collected in order to obtain good repeatability of measurements [9, 10, 16].

Airborne Particulate Matter

Before introduction of automobile catalysts, Pt was not detected in air samples in the USA and Europe [11]. The study of Pt concentrations in airborne particulate matter (PM) in Germany shows that there was a 46-fold increase in Pt concentrations from 1988 to 1999 [18]. In the framework of a multi-tasked project on the risk posed by the emission of PGE from car catalytic converters, systematic campaigns for *PGE* monitoring in air were performed from 1998 to 2000 in selected European countries [19]. Determination of *PGE* in atmospheric aerosols is particularly important in relation to human health because molecules of these metals can penetrate the human body via the respiratory tract (fraction <10 µm). Aerosols that originate in the surrounding air mainly consist of [22]:

- inorganic ions (*e.g.* ammonium, chloride, carbonate, nitrate and sulfate ions; 43%)
- organic compounds (19%)
- water (19%)
- soot (15%)
- various compounds containing metal ions (4%).

The simplest way to sample airborne particulate matter for *PGE* analysis is to pump a known volume of air (10-80 m^3) through a filter for 24 to 72 hours. In most studies airborne particles were collected by means of a sampler equipped with a rotary pump (operational parameters: from 1 m^3/h to 1800 m^3/h, 24/48 h) and 0.8 µm cellulose filter [11, 17, 21, 22]. Determinations of *PGE* in samples with known particle size distribution can be conducted by means of a compactor (cascade or regular

Table 1. The amount of PGE in environmental matrices exposed to vehicular traffic

Sample type	Sampling site	Analytes	Examples of concentration levels in environmental samples	Unit	Average Daily Traffic/ Experiments parameters	Literature cited
1	2	3	4	5	6	7
SOIL	Knittelfeld, Austria	Pt	1.13-32.4	ng/g	20 182	[7]
		Pd	0.90-6.77			
		Rh	0.17-3.11			
		Ru	0.12-5.77			
		Os	0.08-2.36			
		Ir	0.09-0.89			
	Rankweil, Austria	Pt	2.89-134	ng/g	22 072	
		Pd	0.79-24.5			
		Rh	0.40-13.2			
		Ru	0.01-0.89			
		Os	0.03-0.25			
		Ir	0.04-0.15			
	Südost-Tangente, Austria	Pt	2.01-38.9	ng/g	56 679	
		Pd	0.86-6.41			
		Rh	0.15-3.39			
		Ru	0.07-0.55			
		Os	0.04-0.08			
		Ir	0.09-0.24			
	between São Paulo and Jundiaí, Brazil	Pt	0.31-17.4	ng/g	30 000	[8]
		Pd	1.1-58			
		Rh	0.07-8.2			
	Perth, Australia	Pt	30.96 ± 2.13	ng/g	30 500	[16]
		Pd	13.79 ± 0.74			
		Rh	3.47 ± 0.07			
		Pt	68.65 ± 1.20		41 100	
		Pd	69.43 ± 3.85			
		Rh	14.54 ± 1.40			
		Pt	153.20 ± 0.01		29 500	
		Pd	100.06 ± 4.77			
		Rh	26.55 ± 0.83			
		Pt	130.65 ± 4.79		100 000	
		Pd	91.36 ± 6.04			
		Rh	25.18 ± 4.19			
		Pt	107.49 ± 9.53		80 000	
		Pd	108.45 ±1.60			
		Rh	12.47 ± 0.05			
ROAD DUST	Białystok, Poland	Pt	34.2 – 110.9	ng/g	30 000	[10]
		Pd	32.8 – 42.2			
		Rh	6.0 – 19.7			
	Perth, Australia	Pt	53.84 ± 0.88	ng/g	30 50	[16]
		Pd	58.15 ± 1.20			
		Rh	8.78 ± 0.83			
		Pt	161.24 ± 33.47		41 100	
		Pd	132.72 ± 12.10			
		Rh	31.47 ± 7.68			
		Pt	123.64 ± 2.46		25 200	
		Pd	168.48 ± 17.17			
		Rh	24.48 ± 1.20			
		Pt	229.60 ± 9.48		51 000	
		Pd	150.10 ± 9.53			
		Rh	45.10 ± 1.20			
		Pt	224.42 ± 14.27		35 500	
		Pd	293.53 ±3.30			
		Rh	42.72 ±1.80			

Table 1. continued

1	2	3	4	5	6	7
ROAD DUST	Perth, Australia	Pt Pd Rh	261.68 ± 6.78 224.33 ±14.05 56.03 ± 5.77	ng/g	29 500	[16]
		Pt Pd Rh	181.26 ± 31.30 211.74 ± 1.88 44.98 ± 5.03	ng/g	12 000	
		Pt Pd Rh	419.41 ± 25.06 440.46 ± 43.01 91.40 ± 7.86	ng/g	55 000	
		Pt Pd Rh	141.55 ± 28.31 114.45 ± 23.33 22.48 ± 0.37	ng/g	22 500	
	London Orbital motorway	Pt	101.6-764.2	ng/g	85 000 – 145 000	[10]
TUNNEL DUST	Białystok, Poland	Pt Pd Rh	4.17 – 23.3 3.10 – 23.9 6.76 ± 1.28	ng/g	28 000	[9]
GRASS	Białystok, Poland	Pt Pd Rh	8.27 ± 8.98 3.2 ± 0.23 0.63 – 0.68	ng/g	20 600	[9]
AIRBORNE PARTICULATE MATTER	Mong Kok, China	Pt	14-38	pg/m^3	40 000	[11]
	Small village 40 km north of Rome, Italy	Pt Rh	< 0.5 < 0.5 – 0.7	pg/m^3	100	[12]
	Rome, Italy	Pt Rh	2.8 – 40.4 1.6 – 9.4	pg/m^3	30 000 – 40 000	
		Pt Rh	10.0 – 28.6 2.4 – 5.8	pg/m^3	30 000	
		Pt Rh	9.0 – 60.1 1.2 – 8.2	pg/m^3	40 000 – 50 000	
		Pt Rh	2.4 – 18.8 0.8 – 6.8	pg/m^3	20 000	
		Pt Rh	3.4 – 35.8 1.6 – 8.8	pg/m^3	40 000 –50 000	
		Pt Rh	7.8 – 52.0 1.8 – 8.5	pg/m^3	100 000	
EXHAUST FUMES	-	Pt Pd Rh	0.12 – 12.80 0.30 – 5.20 0.23 – 1.5	µg/L	fraction > 0.45 µm aged catalyst (Pt/Pd/Rh)	[13]
	-	Pt Pd Rh	1.28 – 62.2 1.5 – 21.8 0.7 – 12.4	µg/L	fraction > 0.45 µm fresh catalysts (Pt/Pd/Rh)	
	-	Pt Pd Rh	0.14 – 6.85 0.20 – 4.90 0.04 – 2.01	µg/L	fraction > 0.45 µm fresh catalysts (Pd/Rh)	
	-	Pt Pd Rh	0.11 – 36.2 0.013 – 2.8 0.032 – 5.36	µg/L	fraction > 0.45 µm fresh catalysts (Pt)	
	-	Pt	3 – 135 4 – 203 3 – 33	ng/m^3	new catalysts medium age catalysts old age catalysts	[4]

type) [11]. In workplaces passive dosimetry can also be used.

Soil and Benthic Sediments

Samples of soil and benthic sediments (including wastewater sediments) have a complex composition that can be compared to the matrix of road dust [23]. Generally *PGM* show little mobility in soils under natural conditions. However, evidence suggests that certain *PGE*-species bound to soil particles could be remobilized and thus enter the food chain through uptake by plants [7, 24]. Results of the large amount of investigations confirmed significant accumulations of Pt, Pd and Rh and showed characteristic distribution patterns. Concentrations decreased to natural background levels within a few meters from the edge of the traffic lane and within a few centimeters from the soil surface [7]. Furthermore, the examination of relationships between *PGE* and traffic density, vehicle speed and concentrations of common vehicle-derived contaminants (eg. Pb, Cd, Zn) accumulated in roadside soils shows strong correlations [25]. Soil samples for determination of platinum group elements are collected from various depths ranging from 0 to 5 cm [26, 27]. Samples are taken at different depths to obtain information about mobility of these elements.

The *PGE* are emitted in a particulate form [28], the first sink after entering an aquatic biotope is the sediment, where these metals accumulate [29, 30]. Depending on the scope of a study various equipment is employed, ranging from the simplest dredges that scrape sediment from the bottom (resulting samples have the changed internal structure) to specialized samplers with a complex technical design. [31]. McConnell presents the collection procedure, which involves landing a float-equipped helicopter on the lake surface and dropping a weighted tubular sampler fitted with a nylon rope for retrieval. A butterfly valve in the bottom of the tube opens upon impact with the sediment and closes upon retrieval, trapping the contained sediment [32]. The parameters such as sediment color and composition, pH value, redox potential, conductivity and the color of water overlaying the sediment have to be considered in the sampling procedure [30, 32]. Samples of soil and sediments for *PGE* determinations are usually stored in polyethylene (*PE*) or Teflon (polytetrafluoroethylene, *PTFE*) containers.

Water Samples

In order to determine the content of platinum group elements in water it is necessary to obtain samples ranging from a couple to tens of milliliters; the sample volume depends on the scope of analysis. Samples should be collected into completely tight containers that had been previously cleaned by soaking in 0.1 M hydrochloric acid and washed with deionized water. It is critical to avoid trapping air bubbles; otherwise, some analytes may diffuse into the gaseous phase [31] (*e.g.* Ru and Os compounds). To collect water samples at a certain depth samplers operated by remote control and attached to a wire marked at specified length intervals are used [31]. Water samples are usually filtered through a membrane of 0.45 μm pore size, acidified to 0.1% (v/v) with concentrated acid and stored frozen until analysis [33]. Samples should also be analyzed not later than a couple of days after their collection [34]. This is critical because of the possibility of adsorption of metals on the walls of glass and polyethylene sampling containers, which may lead to the loss of analytes.

Biological Samples

Determination of Pt concentrations in biological samples such as saliva, urine, blood and tissues allows the estimation of exposure to *PGE*. Collecting urine samples is rather easy, although even such a simple procedure requires that rules be followed, as specified below [4]:

- persons from whom samples are collected should obey the rules of personal hygiene
- sampling time should be thoroughly considered as to be representative of a certain exposure time; therefore a 24-hour sampling cycle has been recommended
- it is advised to store each sample in polyethylene containers, which should first be decontaminated overnight with 10% HNO_3, then rinsed several times with high purity deionised water [35]
- possible sample contamination should be particularly avoided; this problem is critical in cases of platinum determinations in persons not exposed to this metal
- samples should be stored frozen.

Blood samples could be collected after 2–10 h of infusion of cisplatin, with a hypodermic syringe by vein puncture and kept at -4°C before analysis [36]. Samples of vegetation for *PGE* analysis should be collected with the use of ceramic tools, *i.e.* forceps and scissors. The samples of tissues could be taken with the aid of stainless steel scissors and forceps which had been previously cleaned with 1% ammonium-EDTA-solution and bi-distilled water [37].

Sample Preparation for Analysis

The final determinations of Platinum Group Elements by employing specific analytical techniques can be conducted after proper sample preparation, that is:

- sample mineralization
- extraction and enrichment (preconcentration) of analytes.

Acidic Mineralization

Digestion of solid samples is the first step in the preparations preceding the final measurements. Moreover, in case of voltammetry, the liquid sample should be decomposed (*e.g.* by acidic dissolution) in order to minimize carbon content. Acidic decomposition might also be required before certain types of enrichment procedures.

Acidic mineralization can be performed in Teflon or quartz dishes because both these materials are resistant to high pressure and temperature. Wall memory effect in the mineralization dish is a critical problem. Quartz dishes are characterized by the low wall memory effect [38] as compared to those made of Teflon; Teflon dishes can be used for samples containing similar amounts of *PGE*. In all cases, it is necessary to include a sample blank [4].

High-pressure decomposition systems and microwave heating are incorporated in digestion procedures. The use of high-pressure systems and microwave heating significantly accelerates the decomposition of the samples and leaching analytes [39].

The following rules should be followed during the dissolution stage [14]:

a) the choice of digesting mix should be suitable for the further steps of analysis because, among other things, some elements of the analytical equipment might be prone to reacting with the mix components, such as ingredients of aqua regia or hydrofluoric acid;
b) the composition of dissolving mix should be established for each of the analyzed Platinum Group Metals;
c) mineralization should not be conducted in open dishes because it may lead to the loss some form of analytes;
d) the evaporation steps should not be conducted at temperatures exceeding 100°C; otherwise, loss of analytes may occur. Evaporation to dry mass should be avoided; and
e) the weight of sample to be digested should be chosen adequately to the expected concentrations of analytes and to the size of dish in which mineralization will take place, (in case of soil, dust and biota, a typical sample size for mineralization procedure is 5 g).

The application of the carefully chosen mix of acids is particularly critical in case of Pt and Rh determinations by voltammetric techniques. In this case, mineralization has to be performed in the mix of nitric and hydrochloric acid. Because the nitric acid residue disturbs voltammetric measurements it has to be evaporated after the mineralization step, and the sample should be treated with small amounts of sulfuric and hydrochloric acid [5]. This is a particularly important stage of analysis because it might result in a significant loss of platinum. Accordingly, recovery experiments are very important [40].

Table 2 shows literature data on mineralization/extraction procedures of environmental samples containing Platinum Group Metals.

Separation and Enrichment of Platinum Group Elements

Due to the low or even very low concentrations of *PGE* in environmental samples it is often not possible to make direct determinations of these metals by employing the known analytical techniques; therefore, a preconcentration step becomes necessary. The following approaches can be used [14, 39, 52]:

- liquid-liquid extraction
- solid phase extraction
- techniques based on ion exchange
- electroprecipitation.

For all the above techniques, it is essential to estimate a recovery coefficient for each analyte.

Extraction Techniques

Liquid-Liquid Extraction (LLE)

Liquid-liquid extraction has a broad and well-founded application as both a separation and preconcentration method. This technique can also be used for separating *PGE* from solutions. Because Platinum Group Elements form complexes very easily, solutions of organic complexing agents are often used to facilitate their extraction [52]. The most frequently used solvents are [53-57]:

- methyl-isobutyl ketone
- ditizon
- dibutyl sulfide
- tributyl phophate
- trialkylphosphine oxide
- chloroform.

The antipyrine derivatives of Pt, Pd, Ir and Os are also used for their preconcentration in chloroform [14]. This technique has its limitations due to time consumption and the repeated extraction step which is necessary to secure a good recovery of the analytes.

Solid Phase Extraction (SPE)

Solid phase extraction is a useful procedure for preconcentrating the analytes, including *PGE*. *PGM* complexes can be separated in case of the metals whose ligands show a strong affinity to non-polar stationary phase. Silica gel modified with C_8 or C_{18} groups and polymeric resins based on polystyrene or polystyrene-divinylbenzene are used as sorbents [52]. Complexing agents such as dithiocarbamate are employed in enrichment of *PGE* via solid phase extraction; however, their application remains limited to slightly acidic or neutral solutions in which no oxidation occurs [14].

Techniques Based on the Application of Ion Exchange

The propensity of *PGE* for forming complexes in solutions of mineral acids has been used for, among other things, separating these metals by the techniques based on ion exchange. Platinum Group Elements form stable anionic chlorine complexes, while the majority of transitional group or rare-earth elements form weaker anionic or cationic complexes. The high affinity of *PGE* chlorine complexes for strongly basic anion-exchange resins as well as their weak affinity for cation-exchange resins can be used for separating these metals from sample matrix [52]. In literature, various procedures of *PGE* elution have been described that consider a recovery of analytes, separation efficiency of these metals from the matrix components, and background values [20, 58, 59].

Table 2. Specific information based on literature review in regard to mineralization/extraction procedures and final determination techniques for Platinum Group Elements.

Analytes	Sample type	Extraction conditions	Type of separation/determination technique	Detection limit	Literature
1	2	3	4	5	6
Pt	Aerosol	1. Mineralization of shredded sample-containing filter with the assist of microwave radiation (630 W, aqua regia) 2. Repeated mineralization as in step 1, after cooling down the solution and adding another portion of aqua regia 3. Filtration 4. Evaporation in a rotational evaporator at 80°C 5. Sample dilution	*ICP-DRC-MS*	Pt: 0.5–0.7 pg/m^3	[11]
Pt, Rh	Airborne particulate matter, road dust (fraction < 63 µm)	1. Heating the sample on filter to 450°C 2. Mineralization with a microwave treatment (aqua regia; aqua regia and HF; aqua regia and $HClO_{4;}$; or aqua regia, HF and $HClO_4$ mix) 3. Sample dilution with HCl 4. Storage in PE containers in a freezer	*Q-ICP-MS* *ICP- SF MS* *DP-CSV*		[41]
Pt	Airborne particulate matter, urine	Airborne particulate matter: 1. Sampling with a sampler equipped with polycarbonate filter (0.8 µm, 47 mm, Millipore) for about 4 h 2. Mineralization with a microwave treatment Urine: 1. Addition of H_2O_2 and sulfuric acid to the sample followed by UV-light photolysis	*AdV*	1. Pt: 0.5 pg/m^3 2. Pt in 0.5 ml urine: 1 ng/L	[42]
Pt, Pd, Rh	Road dust	1. Drying (100°C) 2. Homogenization and sieving (fraction < 75 µm was analyzed) 3. Mineralization with a microwave treatment (250~600 W; HCl, HNO_3 and HF), repeated 4 times 4. Evaporation and dissolution of dry residue in HCl	Pt, Rh, Pd: *HR-ICP-MS* Pt, Rh: *Q-ICP-MS* Pd: co-precipitation with Hg/*TXRF*	HR-ICP-MS: Pt: 0.13 pg/ml Rh: 0.05 pg/ml Pd: 1.18 pg/ml Q-ICP-MS: Pt: 16.3 pg/ml Rh: 5.2 pg/ml	[17]
Pt	Road dust	1. Air-drying, weighing and sieving of samples (fraction <2 mm was used in analysis) 2. Ashing at 550°C 3. Distillation 4. Filtration 5. Evaporation 6. Dissolution of dry residue in HNO_3 7. Storage in PE containers	*ID-ICP-MS*	Pt: 0.1 µg/kg	[43]
Pt	Road dust	1. Drying (110°C) 2. Fractionation into three particle sizes (75, 75-125, 125-250 µm) by shaking through a series of test sieves 3. Mineralization with a microwave treatment (aqua regia) 4. Addition of HCl and repeated mineralization 6. Cooling down and evaporation 7. Dissolution of dry residue in aqua regia and deionized water	*ICP-MS*	Pt: 0.12 ng/ml	[16]
Pt, Pd, Rh	2. Soil, road dust 1. Benthic sediment	1. Drying (50°C) 2. Sieving (fraction < 63 µm was used for analysis) 3. Mineralization with a microwave treatment (aqua regia) 4. Filtration through a 0.45 µm filter; filter washing with HCl 5. Sample evaporation in a PTFE dish 6. Dissolution of dry residue with HCl; sonication of the solution	Dowex AF50W-X8 / *ICP-MS*	-	1. [16] 2. [44]
Pt, Rh, Pd	Soil (0-2 cm) (2-5 cm) (5-10 cm)	1. Drying (40°C) and comminuting of the sample 2. Sieving (fraction < 2 mm was used for analysis) 3. Drying (105°C) 4. Ashing (450°C)	Fire assay/*ICP-MS*	Pt & Pd: 0.4 µg/kg Rh: 0.1µg/kg	[45]

Table 2. continued

1	2	3	4	5	6
Pt	Soil	1. Drying (40^{o}C) 2. Sieving (fraction <2 mm was used for analysis) 3. Comminution 4. Mineralization with a microwave treatment (aqua regia) 5. Cooling down, filtration and filling up with deionized water	*ICP-MS*	Pt: 7.6 ng/L	[46]
Pt, Pd, Rh	Soil	1. Drying (40^{o}C) 2. Ashing (450^{o}C) 3. Extraction with a microwave treatment (aqua regia) 4. Evaporation and dissolution in aqua regia 5. Filtration through a PTFE 0.45 μm pore size filter; almost dry evaporation of the filtrate 6. Separation of *PGE* from the matrix via co-precipitation with tellurium and $SnCl_2$ 7. Filtration through a PTFE 0.45 μm pore size filter; filter washing with HCl 8. Dissolution of dry residue in aqua regia; evaporation and addition of HNO_3	*ICP-MS*	Pt: 0.043 ppb Pd: 0.088 ppb Rh: 0.016 ppb	[47]
Ru, Rh, Pd, Os, Ir, Pt	Soil	1. Drying at ambient temperature 2. Sieving (fraction < 2 mm was used for analysis) 3. Measuring sample pH and conductivity; determination of TOC, TC and TIC 4. Drying (105^{o}C) and homogenization 5. Mineralization (300^{o}C; aqua regia) 6. Centrifugation of non-soluble residue 7. Evaporation; addition of HCl; and filtration through a 0.45 μm pore size filter 8. Preconcentration of analytes on cation-exchange column on-line with ICP-MS	*ICP-MS*	-	[7]
Pt	1. Wastewater 2. Wastewater sediment	Wastewater: 1. Sample stabilization with HCl 2. Mineralization at 320^{o}C and under high pressure (aqua regia) 3. Evaporation of HNO_3 at 160^{o}C; addition of HCl Wastewater sediment: 1. Drying (105^{o}C) and grinding 2. Mineralization with a microwave treatment (aqua regia)	1. IV 2. *ICP-MS*	-	[48]
Pt	Hospital wastewater	1. Addition of HNO_3 to the sample until pH 1-2 has been reached 2. Addition of 500 ml 30% H_2O_2 to the 10 ml of sample; sonication 3. Mineralization with UV-light or heating	*AdV*	10 ng/L	[34]
Pt	Hospital wastewater	1. Addition of HNO_3 and HCl to the sample 2. Mineralization (100-130 bar; 300^{o}C) 3. Addition of H_2SO_4 and HCl to the cooled down sample 4. Evaporation of HNO_3 (160^{o}C)	*AdV*	10 ng/L	[49]
Pt	River water Seawater	1. Sample was collected into a PE bottle previously rinsed with HCl 2. Sample filtration onto a 0.45 μm pore size membrane filter 3. Addition of HNO_3; sample stored frozen	*ET-AAS*	0.8 ng/ml	[53]
Pt, Pd, Rh	Snow	1. Pump filtration of thawed snow through a 0.45 μm cellulose filter 2. Ashing of the sample-containing filter 3. Dissolution of dry residue in aqua regia 4. Preconcentration of analytes via co-precipitation with mercury	*GF-AAS*	Pt: 1.0 ng/L Pd: 1.0 ng/L Rh: 0.5 ng/L	[51]

Ion exchange technique is very suitable for eliminating spectral interference in the determinations of *PGE* by *ICP-MS (inductively coupled plasma mass spectrometry)* [52]. However, its disadvantage is that recovery is non-repeatable (it depends on sample type) and the method cannot be used for concurrent separation of all platinum group metals [14].

Cation Exchangers

At present, broad investigations on the application of cation exchange to *PGE* separation are conducted, all dealing with resins characterized by strong cationic features. Separation by cation exchange takes place when an anionic chloro complex of *PGE* passes through a cationic column, while other metals in the sample get quantitatively absorbed on a sorbent bed. High recovery of *PGE* is achieved when a mix of acids is used as eluent. The main obstacles in the application of cation exchange are [14, 60, 61]:

- relatively large amounts of resin necessary to absorb non-*PGE* metals, which results in tedious cleaning of the sorbent bed and high consumption of acids
- relatively large eluent volume necessary for quantitative elution of *PGE* from the column; this increases the risk of concurrent elution of other metals that do not form strong cationic complexes
- difficulties in separating Platinum Group Elements due to the limited amount of eluent used in order to avoid concurrent washing out of other substances from sorbent
- low separation efficiency for Hf and Zr, which may give rise to many problems during the *PGE* determination step via *ICP-MS* and *NA (Neutron Analysis)*. Both metals tend to form stable anionic complexes; this propensity depends on sample type and dissolution technique, and in particular is observed in samples that decompose with the use of hydrofluoric acid.

Anion Exchangers

Regarding the exclusively low concentrations of platinum and palladium in the environmental samples (ng/g, pg/g) the anionic exchangers appear to be preferable to the cationic exchange resins, because they demand a column of a smaller size and smaller volumes of the eluates [62, 63]. Selectivity of anion exchangers is better because of the formation of stable ion pairs between chloro complexes and a sorbent's active groups. The tendency for the metal-chloro complexes to form ion pairs with anion-exchangers is: $[MCl_6]^{2-} > [MCl_4]^{2-} >> [MCl_6]^{3-} >$ aquo species, where M is a metal [59].

Mixtures of different solvents are used for elution, as follows [14, 52, 64-66]:

- To elute $PdCl_4^{2-}$ and $PtCl_4^{2-}$, which bind strongly to some resins, perchloric or concentrated nitric acid are used as they have higher affinity for a given resin.
- To elute platinum and palladium complexes, which are adsorbed too strongly to be eluted from stationary phase, hot concentrated mineral acids or hot ammonia solution also is applied; this results in resin dissolution, which has a negative effect on the removal of contaminating substances and, in turn, *PGE* determinations.
- In order to efficiently remove *PGE* from a resin, a complexing reaction with thiocarbamide or other suitable complexing agent is used.
- To elute *PGM* from anion-exchange resins the thiourea in 0.1 M hydrochloric acid solution is also used.

Similarly to cation exchangers, the separation of Hf and Zr is not complete; however, this problem can be solved by eluting disturbing substances with an HF-HCL mix [64].

Coprecipitation

Reductive coprecipitation with a suitable collector is applied to separate noble metals from base elements and to concentrate them to the level appropriate for instrumental techniques [32]. This method can be used for environmental and biological samples. In such a case, it is necessary to choose the proper sample dissolution procedure. Commonly used precipitating agents are [14, 52, 67, 68]:

- solution of Te, Se, As or Cu salts. $SnCl_2$ is a reducing agent (precipitate is dissolved in nitric acid and the obtained solution can be processed by means of various techniques depending on the required measurement sensitivity);
- mercury nitrate. In this case, mercury is reduced with formic acid (this procedure can be used for palladium enrichment in samples of urine, plants and road dust after high pressure mineralization).
- thiourea and thioacetamide. Both compounds can be applied in coprecipitation of *PGE* with the use of copper collector.

Coprecipitation applied as an enrichment technique is frequently associated with low recovery of analytes therefore, a consecutive use of isotope dilution mass spectrometry (*IDMS*) is recommendable in order to obtain reliable measurements (except in the case of monoisotopic Rh) [69].

Electroprecipitation

Electroprecipitation has found a limited application as a separation/preconcentration technique for the Platinum Group Elements. The application of this method requires samples in liquid phase [14]. During electrochemical preconcentration step analyte ions are separated from the sample matrix and deposited on the electrode. The analytical signal is then obtained during the dissolution of the metal from the electrode. The effectivity of preconcentration and dissolution steps could be influenced by oxygen, surface-active compounds, and inert salts present in a sample [70]. Although, in spite of the high pre-concentration factors and good selectivity of electrodeposition, the efficiency process considerably depends on pH. Under the given conditions (acidic pH, negative potentials), hydrogen ions are reduced and the evolution of hydrogen decreases analyte reduction efficiency [52]. In literature, there is a description of platinum determination technique based on electroprecipitation on a graphite rod, and the final measurements by means of *GF-AAS* (detection limit of about 0.3 ng Pt) [71].

Analytical Techniques Employed for Detection and Quantitative Determination of *PGE* / General Characteristic of Techniques Used for *PGE* Determinations in Environmental Samples

Determination of *PGE* analytes can be performed by means of different analytical procedures; however, the concentration of the metals dictates the choice of technique to be adopted. Fig. 3 shows a schematic presentation of the techniques, which are the most often used for determination of Platinum Group Elements at various concentration levels in environmental samples.

The basic information on analytical techniques used for final determination of *PGE* analytes in environmental samples is presented below.

Gravimetry and Titration Analysis

Gravimetry and titration analysis are widely used for accurately checking and confirming the concentration of standard solutions and in the analysis of *PGE*-rich samples at the content level of 0.1% or higher [72-74]. The main sources of error are losses during precipitation, cleaning of the residues and drying (when gravimetric techniques are used).

UV/VIS Spectrophotometry

The availability of spectrophotometric apparatus and the simplicity of analytical procedures make the technique very attractive for a wide range of applications. The determination of *PGE* by spectrophotometric methods requires their quantitative transformation into soluble stable species that can make the basis of the detection. The use of spectrophotometric methods in *PGM* analysis is limited due to low sensitivity. It is caused by a high chemical similarity of *PGM* resulting in the formation of complexes of similar compositions and properties [75]. However, many new highly specific and sensitive organic reagents are being synthesized and various highly sensitive methods are being developed with molar absorptivities of 10^5–10^6 or even higher [76]. Nevertheless, the use of this method is limited to metallurgical or industrial samples containing *PGE* at μg/g or higher levels [52].

Inductively Coupled Plasma-Atomic Emission Spectrometry (*ICP-AES*)

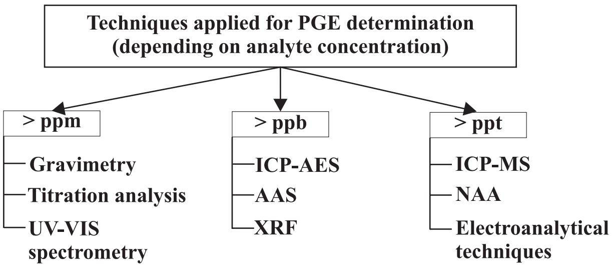

Fig. 3. Analytical procedures employed for determining *PGE* in environmental samples.

One of the characteristic feature of this method is the necessity of converting metals into solution before analysis. Optionally stable suspended matter samples may also be analyzed if the nebulizer is properly constructed. The direct analysis of platinum and palladium by *ICP-AES* however is considerably restricted because of the interferences of the matrix elements, which exist in the samples in concentrations four to eight orders higher than platinum metals [39]. For example, the influence of aluminium and iron on the Pt signal, and iron and vanadium on the Pd signal (due to spectral interferences), has been observed [63]. The low concentrations of Pt and Pd in the environment and the necessity to minimize the spectral and matrix interferences have led to the development of various procedures for isolation and concentration of *PGE*, but ion-exchange is most frequently used. *ICP-AES* has been utilized for the determination of *PGE* in road dust and plant samples (from ng/g to μg/g) after separation on Dowex 1-X10 anion-exchange resin [63, 66]. The technique is also sufficiently sensitive for the determination of noble in sewage sludge and geological samples [76].

Atomic Absorption Spectrometry (*AAS*)

Atomic absorption spectrometry is both an easily available and widely used technique for the determination of platinum group metals in different materials. This technique, similar, to *ICP-AES*, requires total dissolution of the element.

In *FAAS (Flame Atomic Absorption Spectrometry)* the nebulized sample is introduced into flame. The absorption of the analyte atoms is compared against known standards. The following flammable gases are used in *PGE* determinations:

- acetylene/air (Pt, Pd, Ru)
- nitrous oxide and acetylene mix (Rh, Ru).

The main disadvantage of *FAAS* for PGE determination is its poor sensivity. Therefore, the *FAAS* technique generally finds use for noble metals determination in concentrates and PGM-rich samples [51, 78].

In *GFAAS (Graphite Furnace Atomic Absorption Spectrometry)* analysis, usually a small volume of sample solution or solid sample, is dispensed into a graphite atomizer and the absorption of the produced atoms is measured against standards. Sensitivity of *PGE* determinations by *GFAAS* mainly depends on the metal's melting point. The

GF-AAS determination of *PGE* requires high atomization temperatures due to the high vaporization temperature of the *PGM* compounds [79].

Measurements can be disturbed by the presence of other noble metals due to the formation of alloys, and by other elements that are present in environmental samples, *e.g.* Ni [80]. With the aim of the *GF-AAS* analysis of platinum in catalyst, vegetation, soil and water samples, the matrix effect from excess concentration of several ions (eg. Pb^{2+}, Cu^{2+}, Ca^{2+}, Co^{2+}, ClO_4^-, Fe^{3+}, Fe^{2+}, Al^{3+}, Sn^{2+}, Rh^{3+}, Zr^{4+}, Ce^{4+}, Pd^{2+}) on the Pt signal was studied. The tolerance limits found show that platinum can be determined in the presence of a variety of ions [33]. In overcoming some of the interferences, operations such as separation and preconcentration of analytes prior to *GFAAS* determination, standard additions and also background correction using continuum source are useful.

The method is used for Pt and Pd measurements in spiked tap and wastewater and road dust samples [80-83]. *GFAAS* detection also has been employed for the estimation of *PGM* in soil [84] and snow samples [51].

X-ray Fluorescence Spectroscopy (*XRF*)

X-ray fluorescence spectrometric method is generally not directly suitable for the determination of trace concentrations of *PGE* in environmental samples, thus there appear to be only a few examples of the application of XRF in PGE analysis in published literature. The technique has been used for analysis of total platinum concentrations in body fluids of patients treated with the antitumor drug cis-dichlorodiammineplatinum (II) [85]. Minimum detection limits range from 0.10 to 0.25 g Pt per ml, depending on body fluid. The X-ray method has been recognized as a suitable technique for the determination of Pt and Rh in automotive catalyst samples [84]. X-ray technique has also been reviewed for the determination of PGE in corrosion-resistant steels [86].

Inductively Coupled Plasma-Mass Spectrometry (*ICP-MS*)

Inductively coupled plasma–mass spectrometry (*ICP–MS*) is potentially suitable for analysis of PGEs, because of its extremely low *DL (Detection Limit),* multielement capabilities and wide linear dynamic range (five to six orders). *ICP-MS* has been recognized as a widely applied technique for the determination of *PGE* both in environmental [10, 16, 87-89] and biological samples [90-93].

However, this technique has the disadvantage of possible spectral overlap from isotopes of different elements and, more commonly, the formation of molecular ions inside the Ar plasma, which can give rise to isobaric interferences in the mass spectra. Spectral type disturbances during the determinations of Pt, Pd, Rh and Ru are caused by $^{179}Hf^{16}O$, $^{178}Hf^{16}O$ (^{194}Pt) (^{195}Pt), $^{40}Ar^{65}Cu$, $^{89}Y^{16}O$, $^{87}Rb^{18}O$ (^{105}Pd), $^{40}Ar^{63}Cu$, $^{36}Ar^{67}Zn$, $^{206}Pb^{2+}$, $^{87}Sr^{16}O$, $^{87}Rb^{16}O$ (^{103}Rh), $^{64}Zn^{35}Cl$ (^{99}Ru), $^{64}Zn^{37}Cl$, $^{66}Zn^{35}Cl$, $^{61}Ni^{40}Ar$, $^{63}Cu^{38}Ar$ and $^{65}Cu^{36}Ar$ (^{101}Ru). No substantial interferences are known for iridium [94]. There are some ways to decrease spectral interferences, such as:

- mathematical correction [43, 95]
- separating analytes from the sample matrix before analysis [94, 44]
- using a mass spectrometer with proper resolution [21]
- employing an alternative way of introducing samples into a measuring system [96].

Non-spectral interferences are more complex as compared to the spectral ones. They may cause signal attenuation or amplification due to the presence of solid particles in solution. The effect of disturbing substances can be alleviated by adding internal standard that has similar chemical properties to the analyte. Detailed studies of the methods of elimination of interferences in determination of platinum and palladium in environmental samples by inductively coupled plasma mass spectrometry have been done by Leśniewska et al. [97].

Neutron Activation Analysis (*NAA*)

Together with *ICP-MS* and *CSV (Cathodic Stripping Voltammetry), NAA* is the most sensitive technique for the determination of *PGE*. It is the method of elemental analysis based on the transition from a stable atomic nucleus (nuclide) into radioactive nucleus (radionuclide) due to irradiation with neutrons, photons or active particles. The radionuclide (radioisotope) decay model is used in qualitative analysis of a given trace element and emitted radiation is proportional to the initial analyte concentration in the sample. From among different types of radiation which can be emitted, it is gamma (γ) radiation that has the best parameters for selective and parallel determinations of *PGE.*

The two variants of *NAA*- instrumental *NAA* (*INAA, Instrumental Neutron Activation*) and radiochemical *NAA* (*RNAA, Radiochemical Neutron Activation*), score over other techniques because of their accuracy, sensitivity and freedom from interference. The interference-free INAA of ^{190}Pt gamma-peak at 538.9 keV suffers from low sensitivity for most environmental and biological samples due to the low natural abundance (0.01%) of Pt [79]. The measurement of ^{190}Pt is limited by its short half-life of 30.8 min, therefore Pt is often determined via ^{197}Pt, or via the ^{199}Au daughter of ^{199}Pt. However, in a variety of environmental and biological samples, ^{24}Na interference with the ^{197}Pt permits analysis only after long decay times. ^{197}Pt also suffers from ^{197}Hg interference [98]. For RNAA, almost all investigation of platinum are done using 199Au as the indicator nuclide. The main disadvantages of RNAA is that it is time-consuming [98].

The *NAA* method has been utilized for the determination of Pt in rock samples after nickel sulphide fire assay preconcentration [99]. The technique also has been used in conjunction with a preirradiation concentration/separation procedure employing a Dowex ion exchange chromatographic column for the determination of low levels of platinum in road dust samples. *NAA* detection has been employed for the estimation of Pt in airborne dust samples. The spectral interferences of platinum were removed by mathematical correction [100].

Electroanalytical Techniques

Techniques based on the electrochemical properties of the analytes are selectively used for *PGE* determination. Among numerous electroanalytical techniques used for the determination of *PGM*, voltametric methods are the most popular ones. The technique is extremely sensitive to the presence of organic matrix constituens. To minimize interference it is preferable to destroy organic matrix to limit the carbon content of the sample solution to under 0.5% and avoid nitric acid prior to analysis. Moreover, an important aspects of *ASV (Adsorptive Stripping Voltammetry)* analysis is the deposition time, for which cautious optimization prevents interference from H_2 bubbling. A reduced deposition time is a prerequisite for the measurement of higher concentrations of Pt [79, 101].

Due to its high sensitivity for this metal, ASV methods have been widely used for the analysis of Pt in various matrices, including biological materials [92]. With this technique trace levels of Pt in hospital sewage water [5, 34] plant material [102], animal tissues [103] and another selected environmental and biological samples (soil and garden mould, vegetables, foodstuffs, fertilizers, fuels [104] were analysed. This method has also been applied for assessment of occupational exposure by selective determination of platinum in workroom air and in blood and urine samples from medical staff nursing cancer patients [105].

Summary

Despite increasing knowledge about the concentrations of Platinum Group Elements in environmental samples it is still difficult to estimate what effects can be caused by them in the environment. Although present emissions of *PGE* do not pose a serious threat, the growing number of motor vehicles equipped with catalytic converters and accumulation of Platinum Group Metals in the environment may become a problem in the near future. Therefore, it is important to conduct ongoing monitoring of these elements in environmental as well as biological samples. Analyzing *PGE* in such sample types creates a serious challenge for scientists. In particular, *PGM* occur at very low concentrations and there are no suitable reference materials, which makes validation of the existing analytical procedures very difficult.

Acknowledgements

This scientific work was financially supported as a research project (1T09D 098 30).

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