Review

Methods for the determination of platinum group elements originating from the abrasion of automotive catalytic converters

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Abstract

Anthropogenic emission of platinum group elements (PGEs) from the abrasion of automotive catalytic converters into the environment has significantly increased. However, the concentration level of these PGEs (i.e. Pd, Pt, Rh) is still very low in the nature. Accordingly, their determination and speciation in various environmental compartments appears to be a challenging task for analytical chemists. The present review gives an overview of the analytical procedures documented in this particular field of analytical chemistry with a distinctive emphasis on spectrochemical methodology, it being the most sensitive and robust for accomplishing the above analytical task.

Keywords: platinum group metals, spectrochemical methods, electroanalytical methods, analytical methodology, vehicle exhaust catalyst

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Contents

1. Introduction

Platinum group elements (PGEs) play a decisive role in the performance of exhaust systems, worldwide applied in vehicles and in some household utensils, to reduce the emission of gaseous pollutants, such as carbon monoxide, nitrogen oxides, and hydrocarbons [1, 2]. However, the hot exhaust gases flowing through the converter cause abrasion/ablation of these units, leading to the emission of the PGEs to the environment. Thus, these novel anthropogenic metals have an increasing impact on nature due to the increasing number of cars equipped with catalytic converters [2]. Moreover, several PGEs and their complex salts (e.g., Pd- and Pt-chlorides) have been reported as a potential health risk to humans, causing asthma, allergy, rhino-conjunctivitis, and other serious health problems [3, 4].

Barbante and co-workers [5, 6] found that Pt concentrations in remote snow cores of Greenland and the Alps have been considerably rising since 1975, and had increased 40-fold till the mid-1990s. The Pt:Rh ratio was found to be very close to that in catalytic converters [6]. Van de Velde et al. [7] also detected increased concentrations of Pd and Rh in the Mont Blanc ice and snow samples, especially over the last decade, whilst no clear enhancement was found for Pt. These PGE polluted places are located at high altitudes and far away from residential areas of heavy traffic, indicating a large-scale contamination impact of the vehicle catalysts, likely through the troposphere of the Northern Hemisphere [5].

In view of the above facts, the monitoring of PGEs originating from the emission of the automotive catalytic converter attrition into environmental samples have paramount importance with respect to estimation of the future risk of the human health and the ecosystem. The concentration of these elements is still relatively low in environmental compartments [1, 2], thus their analysis requires analytical methods of

high sensitivity, selectivity, and the control of interference effects [8]. For overcoming this analytical challenge, only few analytical techniques are directly (i.e., without any previous pre-concentration, and/or separation of the analyte/matrix) applicable. The most appropriate techniques for the determination of PGEs include inductively coupled plasma mass spectrometry (ICP-MS), adsorptive stripping voltammetry (ASV), and instrumental neutron activation analysis (INAA). Total reflection X-ray fluorescence spectrometry (TXRF), inductively coupled plasma atomic emission spectrometry (ICP-AES) and graphite furnace atomic absorption spectrometry (GFAAS) can be applied, but imply prior pre-concentration/matrix-separation steps to assess PGE concentrations at the required ultra-trace levels. Most other techniques are usually handicapped by interferences of various types.

In former reviews of this particular topic, the authors have discussed the methods of determination of PGEs in environmental samples [8-12], the distribution and speciation of PGEs in environmental compartments [13], the possible health risk of anthropogenic PGEs [2, 4], and the transport and bioavailability of PGEs [2]. These topics, together with a number of novel findings in this field, were also discussed in a recent book [1]. The aim of the present review is to evaluate the utility of existing analytical methodology applied for the quantification of PGE ultra-traces in diverse environmental/biological compartments, and to give some predictions on the future trends in the evolution of this field of analytical chemistry.

2. Means of sample preparation

2.1. Storage of samples

Sampling processes, the handling of samples, and the dissolution/digestion procedures have a substantial influence on the accuracy and precision of the analytical

procedures used for the ultra-trace analysis of PGEs. Special precaution is required for the purification of the decomposition agents [14] and the vessels employed to achieve appropriately low blank levels [14, 79]. The proper choice of vessels for the storage of samples has been verified in the case of Pd, as hydrolysis/adsorption occurs for weak acidic conditions on long standing [81]. Similar sorption losses of Pt were observed when utilizing PTFE vessels for digestion [57]. On the other hand, quartz vessels are advantageous for opening up samples [57], and, additionally, they also provide better storage properties and lower blank values, particularly after thiourea plus HCl cleaning pre-treatment [81]. For solutions stored in polyethylene bottles, the Pt concentration showed a drastic fall on standing, whereas this was not detected in polystyrene flasks [40].

2.2. Digestion methods

Several methods have been offered for digestion of PGEs, such as acidic dissolution, fusion methods, the application of chlorination and fire assay (i.e., fusion and collection of PGEs on a metal sulphide, - usually NiS - button, also referred to as "docimasy") procedures [15,120,146,148]. The most common decomposition method is the acidic dissolution, based on the application of aqua regia plus hydrofluoric acid (HF), the latter used only in the presence of silicate matrix constituents. Microwave ovens, high-pressure PTFE bombs and high-pressure ashers (HPAs) are used to decompose a variety of matrices; e.g. road dust, soil, airborne particulate, and biological materials. Accurate analytical results were also obtained without the application of HF for "difficult" silicate-containing matrices (e.g., road dust) particularly via aqua regia leaching under high-pressure and -temperature conditions [41]. Despite this, in some cases, Pd has been reported to strongly bound to silicate

matrices compared to other PGEs, which demands efficient HF digestion procedures [137]. Vaporization of the excess HF can be avoided by addition of boric acid [16]. For biological materials, such as blood samples, mineralization or decomposition by UV photolysis is highly recommended [17], whereas urine can be measured without decomposition of the samples by GFAAS [18], or with UV photolysis by ICP-MS [17, 19]. An overview of the decomposition methods is included in Table 1.

2.3. Pre-concentration and matrix separation methods

In environmental samples, the low concentration of PGEs (below $\mu g\ g^{-1}$ levels) together with the high concentration of interfering matrix components often requires a pre-concentration/enrichment step combined with a matrix-separation. For example, fire-assay procedures can also be used for the dissolution and subsequent precipitation of PGEs with Te and $SnCl_2$ [20-22], whose precipitate can be dissolved again to measure the metals in pre-concentrated solutions. For a more structured overview, the pre-concentration/matrix separation methods are discussed in subsequent sections together with the detection methods (ICP-MS, ICP-AES, TXRF and GFAAS). Table 1 also summarizes the pre-concentration and matrix separation methods.

3. ICP-MS methods

3.1. General

The ICP-MS is one of the most sensitive analytical techniques presently available It is being developed continuously, to increase the sensitivity, selectivity, and capability to process fast transient signals [23]. The latter feature is important from the viewpoint of those sample introduction methods which generate impulse

signals. The "Achilles-heel" of the ICP-MS technique is the means of sample introduction into the plasma, since it decisively affects the extent of spectral ("overlap" or "mass") and non-spectral (matrix) interferences, and hence, the analytical performance. When performing ICP-MS measurements, due to presence of argon plasma gas, matrix and sample, the formation of interfering molecular ions (e.g., argides and oxides) and doubly charged ions takes place in the high temperature plasma source and in the sample extraction unit of the MS, which are subsequently transported to the ion optics and detector [142]. If the mass-to-charge ratio of these species is close to that of the element to be measured, this can result in spectral overlapping and an enhanced analyte signal, which can lead to inaccurate analytical results. The spectral overlap problems in ICP-MS are thoroughly discussed in an extensive review [24]. Perry et al. [85] have also reviewed the application of ICP-MS for the determination of PGEs in geological materials, biological, botanical and water analysis. Non-spectral interference induced by high concentrations of matrix constituents manifests in either suppression or enhancement of analyte signals. In the determination of PGEs, spectral interferences appear to be much significant than non-spectral ones as follows in the next sections.

3.2. Interference effects and their elimination

3.2.1. Spectral overlap interferences

Quadropole ICP-MS (Q-ICP-MS) is a more commonly employed apparatus for the determination of PGEs in environmental samples than the high-resolution (HR) sector field (SF) ICP-MS. The Q-ICP-MS spectrometers possess a mean mass resolution of around 300 m/Δm, whereas the SF-ICP-MS working under HR settings supplies with an enhanced selectivity (7500-11000 m/Δm). Regarding the

interference-free isotopes, SF-ICP-MS operating in low resolution (LR) mode exhibits far better limit of detection (LOD) than Q-ICP-MS [116]. Several studies emphasize the extent of mass-spectral overlap interferences and routes to their possible elimination, as will be subsequently discussed.

Rauch et al. [25] studied the interference effects on the determination of Pd, Pt and Rh in road dust and river sediment samples using SF-ICP-MS with ultrasonic nebulization (UN). Several interferences with the determination of these elements and the minimal resolution necessary to separate the peaks of analytes and interfering ions are presented in Table 2. For ^{103}Rh, both ^{206}Pb^{2+} and ArCu^{+} were found to be the main interfering ions in LR mode, but they could be efficiently separated in the HR mode. The high levels of Zn in environmental samples produce interference by ^{36}Ar^{67}Zn^{+}, which can be successfully removed by applying the HR mode. However, the interference from ^{87}Sr^{16}O^{+} and ^{87}Rb^{16}O^{+} remained. The apparent signal on ^{106}Pd due to interfering Cd^{2+} increased linearly with concentration. Both ^{105}Pd and ^{106}Pd were found to be strongly interfered in LR mode and, according to Table 2, most of the interferences were not removed by increasing the resolution. Additionally, Cu and Rb were also found to be a potential interferent with ^{106}Pd, these effects likely being due to the formation of ^{40}Ar^{65}Cu^{1}H^{+} and ^{87}Rb^{18}O^{1}H^{+}, respectively. For ^{195}Pt, the only interfering ion is HfO^{+}, which was successfully eliminated using exceptionally high resolution, i.e., 10102 m/Δm. The SF-ICP-MS instrument earlier used for this work was restricted to 7500 (m/Δm), which proved to be inefficient for completely removing all interferences.

Petrucci et al. [26] determined Pd, Pt and Rh in urine samples using SF-ICP-MS with UN. Due to the fairly high concentration of Cu, Hf, Rb, Sr, Y and Zn in the matrix, most of the possible interference effects were studied by spiking the sample

solutions with the interfering elements at various concentrations. The influence of $^{87}Rb^{16}O^+$ and $^{87}Sr^{16}O^+$ was found to be negligible on the ^{103}Rh signal, while the effect of $^{40}Ar^{63}Cu^+$ and $^{68}Zn^{35}Cl^+$ had to be taken into account because of the high Cu and Zn concentrations in the roadside dusts, and the high Cl concentration in the sample solutions, due to the digestion procedure with aqua regia. Generally, the contribution of $^{40}Ar^{63}Cu^+$ to the analytical signal was generally 0.001%, whereas no influence from the $^{68}Zn^{35}Cl^+$ ion was observed on the ^{103}Rh signal. For Pd determination, the ^{105}Pd isotope was exclusively used because the other isotopes suffered from interference from several argides and oxides of Zn, Zr and Mo. Furthermore, the presence of Y at high concentrations in the matrix exhibited the strongest interference on ^{105}Pd in the form of $^{89}Y^{16}O^+$.

Begerow et al. applied UV photolysis of urine [19] and blood [17] samples to decompose the organic matrix, which otherwise caused memory effects, blockage of the sample introduction system and signal instabilities with the ICP-MS determination of Pt, Pd and Ir. As regards the spectral interferences, even the maximum resolution of the spectrometer (7500 m/Δm) was not sufficient to resolve spectral overlaps on ^{104}Pd, ^{106}Pd and ^{108}Pd originating from $^{88}Sr^{16}O^+$, $^{90}Zr^{16}O^+$, $^{92}Zr^{16}O^+$, $^{104}Ru^+$, $^{106}Cd^+$ and $^{108}Cd^+$. On the other hand, those from $^{208}Pb^{2+}$, $^{65}Cu^{40}Ar^+$, $^{64}Zn^{40}Ar^+$ and $^{66}Zn^{40}Ar^+$ were completely removed [19]. The presence of $^{35}Cl_3^+$ polyatomic ion (interfering with ^{105}Pd) is evident when analyzing chlorine-containing matrices, such as the blood samples [28], and in those samples which are digested with chloride containing agents (e.g. aqua regia) to stabilize the PGEs in the form of chloro complexes. This interference cannot be eliminated by SF-ICP-MS instrument having maximum resolution of 7500 m/Δm. In HR mode, a significant decrease in sensitivity (to 1% of that found with LR mode) was observed which, accordingly, impairs the LOD [19,

116]. In contrast to Pd, the determination of Pt and Ir in blood samples is not hampered by spectral interferences. The HfO^+ interference on Pt is of no significance because of the low Hf levels in blood [17].

Gomez et al. [29] studied the interference effects of $^{179}Hf^{16}O^+$ on the determination of ^{195}Pt, and the effect of $^{206}Pb^{2+}$, $^{40}Ar^{63}Cu^+$, $^{87}Sr^{16}O^+$ and $^{87}Rb^{16}O^+$ on ^{103}Rh, and also the effect of $^{89}Y^{16}O^+$, $^{40}Ar^{65}Cu^+$ and $^{36}Ar^{69}Ga^+$ on ^{105}Pd in airborne particulate matter having aerodynamic diameter below 10 μm (PM_{10}). The possibilities for alleviating these interferences include the optimization of the nebulizer gas flow rate and the plasma input power. The nebulizer gas flow rate had no effect on the extent of interferences, whereas by using high plasma power settings (1350 W) the analyte-interferent ratios were successfully decreased. An exception was interference by Pb^{2+} formation of which was minimized when using medium plasma power (1150 W).

Quadrupole and SF-ICP-MS techniques were applied to distinguish the role of $^{179}Hf^{16}O^+$ on the ^{195}Pt signal in a large variety of nutrient plants to track the uptake of Pt emitted by automobile exhaust catalysts [33]. The Pt and HfO^+ mass spectra indicated a strong interference effect, which is due to the small mass difference (0.021944 Dalton (Da)) between ^{195}Pt and $^{179}Hf^{16}O^+$. Therefore, a resolution of 8885 (m/Δm) is needed to resolve the two peaks, which is not achievable with the Q-ICP-MS techniques used.

Even such pristine matrices as polar snow and ice could have metal contaminants which give rise to interferences on the PGE determinations [6]. The most significant influence on Rh arise from $^{206}Pb^{2+}$, $^{40}Ar^{63}Cu^+$, $^{14}N^{89}Y^+$ and $^{23}Na^{40}Ar^{40}Ar^+$, for which resolutions of 1248, 8040, 30000 and 11300, respectively are needed. However, determination of Rh could be accomplished under LR

conditions because of the low levels of Rh in the samples demanded the best available LOD, and moreover, Cu, Pb, Zn, Sr, Rb, Y, Na and Zr matrix constituents up to 1 ng g^{-1} did not interfere. For ^{106}Pd, ^{106}Cd$^+$, ^{40}Ar^{66}Zn$^+$ and ^{90}Zr^{16}O$^+$ could be considered as potential interferents based on their concentration in the snow samples and the natural abundance ratios and thus, they were measured with the same multi-element solution as Rh. On the other hand, the main interferent was found to be Cd, causing a linear increase in the ^{106}Pd signal. Increasing Zn, Ge, Sr and Y concentrations had no effect up to 5 ng g^{-1}. For Zr, as an interferent, the high oxide bond strength of ZrO (795 kJ mol^{-1}) yields a fairly high ZrO$^+$/Zr$^+$ ratio (0.0026), and due to this, the apparent blank value was exceeded above ~0.2 ng g^{-1} Zr in the solutions. When studying the interference of HfO$^+$ on ^{195}Pt, a value of 10 ng g^{-1} was found for Hf concentration, implying an HfO$^+$/Hf$^+$ ratio of 0.009.

It is noted that spectra stemming from argon plasma gas and nebulized aqueous solution of sample may be quite complex and that minor isotopic species of this spectra cannot be ignored when determinations are performed at the ultra-trace level [23]. It follows also that uncommon polyatomic interfering ions, (e.g., ArCuH$^+$ and RbOH$^+$ as above [25]) can cause spectral overlapping interferences. For analytical practice, monitoring of all possible interferents originating from the matrix and correction of the analyte concentrations before quantification are recommended to obtain accurate results.

3.2.2. Non-spectral interferences

Non-spectral, or matrix interference effects with the ICP-MS determination of PGEs were studied in connection with the NiS fire assay digestion method [135]. For solutions derived from the latter fusion method, the principal matrix element was

found to be Ni with the other matrix elements occurring at much lower concentration. The ion count of analyte was shown to be dependent on the relative atomic mass and degree of ionization of analyte and matrix element, as well on plasma operating conditions. Using PN for sample introduction, a 50 % signal suppression was found for Pt with the addition of 5000 ppm Ni. When ETV sample introduction with the addition of 500 ppm Ni (as nitrate) was applied enhanced Pd, Pt and Rh signals were observed by factors of 4.5, 9.4 and 8.7, respectively. The enhancements were attributed to an altered vaporization characteristic of PGEs from the graphite surface of the ETV (chemical modification on their vaporization behavior) and an increased transport efficiency of PGEs to the plasma (i.e. reduced adsorption or condensation loss in the ETV and transport conduit surfaces). These effects were found to be equally dominant on the ion counts of PGEs. At Ni concentrations higher than 500 ppm, the enhancement factors decreased (up to 10000 ppm Ni), but still remained significant. This was due to the plasma loading and space charge effects in the ion lens system becoming influential on the ion count rates of analytes. The above study has shown the applicability of docimasy to the determination of PGEs by ICP-MS, which possibility was also utilized in other works [146,148].

3.3. Sample introduction methods

3.3.1. General

The means to overcome mass spectral interference effects during the determination of ultra-trace levels of PGEs include application of solid sample introduction devices; i.e. electrothermal vaporization (ETV) and laser ablation (LA) micro probes to produce dry aerosols (these techniques are also referred as *Thermal Sample Introduction* (TSI) methods [74]), alternative nebulization of the liquid

samples, and application of HR-ICP-MS, are discussed in detail below. Kántor made a detailed and critical assessment of TSI methodology in a recent review [74], whereas the basic concepts of these essential sample introduction techniques were laid down and discussed in an earlier paper [75]. As can be deduced from the previous section, the composition of the matrix, the methods of sample preparation, and the application of pre-concentration/matrix separation can considerably influence the magnitude of interferences. Therefore, these important issues are also considered in detail below, together with detection methods.

3.3.2. Sample introduction by nebulization techniques

Common pneumatic nebulization based techniques such as V-groove or Meinhard nebulizers have an aerosol yield of 1-4% [147]. This efficiency can be increased by more than one order of magnitude using ultrasonic, thermospray, microconcentric, direct injection, or hydraulic high pressure nebulization. These systems also offer the possibility of on-line matrix removal in the desolvator/condensor stages, which is important for the reduction of interferences. By these techniques improvement are observed in the ionization ratio of PGEs, but also for the formation of doubly charged interfering ions (e.g. Pb^{2+}).

Parent et al. [35] measured Pt in "cordierite" (Mg-Fe-Al silicate), the material used as the body of the catalytic converters, in which matrix the Hf traces are known to be present. For studying the HfO^+ interference, standard solutions of Hf were introduced with either pneumatic nebulization (PN) or thermospray nebulization (TN). As an indicator of the extent of interference, the level of oxides was tracked. An oxide-metal ratio of 0.3-0.7% was found for PN, whereas this value was advantageously reduced to 0.2-0.3% for TN. However, the memory effect was higher

with TN than with PN, and there was a need to use Triton X-100 rinsing solution of at least 0.1 % for 2-3 min to completely remove Pt from the nebulizer. Precipitation of HfO$_2$, due to the evaporation of HF at the heated capillary also caused a memory-effect, which was eliminated by adding more HF to the sample solutions.

Lustig et al. [33] found that the size of the droplets issuing from the spray chamber and the plasma temperature decisively affect the amount of HfO$^+$ formed in the argon-plasma. With a cross-flow (gem-type) nebulizer, a 5-10-times lower HfO concentration was observed, compared to a conventional Meinhard-nebulizer equipped with cyclonic spray chamber. Parent et al. [34] used TN for sample introduction into the ICP-MS for the determination of Pt in environmental and biological samples, an approach which improved the LOD by a factor of four compared to conventional PN.

Riepe et al. [37, 38] used a direct injection nebulizer (DIN) with an 'active' silica capillary to remove the HfO$^+$ interference from Pt when analysing car exhaust fumes by Q-ICP-MS. The activation of the fused silica capillary (i.e., production of free silanol groups) was accomplished by sodium hydroxide treatment. In HCl solutions Pt forms a negatively charged complex, but Hf remains positively charged. As a result, the negatively charged surface retained the HfO cations in the capillary, whereas its interaction with Pt complexes was negligible. Obviously, the acid concentration in the sample solutions and the aspiration flow rate can influence the retention of Hf and Pt, the parameters of which need multi-variable optimization. The main goals of this work were to achieve linear calibration curves and a better precision with the use of activated capillaries, whereas with the "non-activated" capillaries, highly non-linear calibration was observed, which is a direct consequence of the HfO$^+$ interference on Pt. The same scheme was applicable to Pd and Rh to

remove the interfering matrix constituents (Cu, Sr, Ba and Pb for Rh, and Y and Cu for Pd) from the sample solutions. The silica capillary was modified with either 3-aminopropyltrimethoxysilane, or 2-(4-chlorosulfonylphenyl)-ethyltrichlorosilane. Atomic force electron microscopic characterization showed that the coverage of the capillary surface is dependent on the impurity content of the host silica and the type of modifying reagent [38]. García et al. [39] also applied modified silica capillary coupled either to a microconcentric nebulizer (MCN), or to a DIN [39] during the Q-ICP-MS determination of Pd in car exhaust fumes and road-side dust. Certainly, for all of these techniques, the capillary has to be flushed after each sample introduction step to get rid of the interfering ions from the ion-exchanger, and to regenerate the column for the next sample, which leads to a disadvantageously prolonged analysis time.

Double focusing ICP-MS fitted with an MCN was applied to determine Rh, Pd and Pt in polar and alpine snow and ice by Barbante et al. [5, 6]. They used a thermostatted spray chamber to reduce the water content of the aerosols and hence, consequent formation of interfering, polyatomic oxo-ions. The ^{106}Pd and ^{195}Pt as the most abundant isotopes of the corresponding PGEs were used for detection purposes, which are feasible for determinations performed in such ultrapure matrices. However, in the analysis of complex matrices, such as soils, they are hampered by a large number of mono- and polyatomic interferences.

Pt, Pd and Rh were determined in road dust samples by SF-ICP-MS using UN coupled with a membrane desolvator [64]. The authors found a HfO^+/Hf^+ formation ratio of 0.02% with this sample introduction, which is a 10-fold improvement compared to the corresponding ratio when using a PN system (0.2%). This methodological advance is important in connection with determination of Pt in

matrices of high Hf trace content, and it also rules out matrix separation, a usually necessary procedure for both isotope dilution (ID) and external calibration methods. For Rh, the interferences from $^{206}Pb^{2+}$, $^{63}Cu^{40}Ar^+$ and $^{66}Zn^{37}Cl^+$ could be successfully eliminated in the HR mode. The isobaric effects of $^{36}Ar^{67}Zn^+$, $^{86}Sr^{17}O^+$ and $^{87}Rb^{16}O^+$ were assessed by the addition of the 2-fold excess of Zn, Sr and Rb to the standard solutions, respectively. For determination of Pd, the ^{105}Pd isotope is generally preferable because it is the less interfered isotope. However, studies with a Sr containing matrix revealed the necessity of a mathematical correction, attributable to the formation of $^{88}Sr^{16}O^1H^+$ interferent (with an abundance of 82.4%) [64]. Other workers also found negligibly small HfO^+ interference on ^{195}Pt when using UN with membrane desolvation for the analysis of tree bark and road dust samples [31].

For sampling of car exhaust fumes, Moldovan et al. [36] used a novel device consisting of a two-step cascade of polyethylene containers with bubblers filled with acidic adsorbent solutions (i.e., modified gas separator vessels), which were immersed in ice baths to condensate most of the water vapor from the exhaust gases. This system allowed drawing a distinction between the soluble and insoluble fractions of PGEs captured in the gas separator flasks, which is essential for the assessment of the bioavailability of PGEs released by automotive catalytic converters.

3.3.3. ETV and spark ablation sample introduction methods

ETV sample introduction methods involve the vaporization of samples from a graphite/metal sample holder by resistance heating and their subsequent transport to the detection source.

In the earliest report, Grégoire [135] examined the feasibility of ETV for the introduction of PGEs to the ICP-MS. The home-made ETV device contained an

electrothermally heated graphite strip (pyrolytically coated) for the deposition and vaporization of the samples. An argon stream was introduced tangentially to the metal supports of the graphite strip, whereas a quartz cover was placed above the vaporization surface to minimise condensation of the sample vapors (i.e., losses), thus maximizing the aerosol transport to the plasma. PGEs behave as refractory elements in the graphite furnace. Therefore, a fast heating ramp and the application of the maximum permissible vaporization temperature (*ca.* 3000 K for graphite furnaces) were recommended to obtain fast transient signals with maximum peak height. The matrix effect of Ni (present from the fire assay digestion step) on Pt was studied. Applying PN, a decreasing count rate of Pt was observed with increasing Ni concentration, whereas using ETV, 500 ppm Ni matrix increased the signals of Pt, Rh, and Pd by around 4-10-fold; these enhancement effects being utilized to increase the detection power of the method [135].

Byrne et al. [47] studied the vaporization and atomization of all the six PGEs utilizing an ETV-ICP-MS tandem technique. A very similar vaporization mechanism was concluded for five PGEs (Ir, Rh, Ru, Pd and Pt), which incorporated first the conversion of the PGE salt to metal in the ETV unit, and then the vaporization of this metallic form. This mechanism was independent of the presence of matrices such as HNO_3, HCl, and $TeCl_2$. On the other hand, for Os, the means of vaporization was found to be strikingly different, and largely depended on the composition of the matrix present. In HNO_3 medium, Os vaporized in two distinct stages, i.e.: (1) volatile Os oxides detectable above 800 ^{o}C; and (2) metallic Os above 2000 ^{o}C, which is a reduction product of the Os oxides. On the other hand, use of a $TeCl_2$ chemical modifier changes this mechanism so that only $OsTe_2$ is vaporized in the ETV at fairly low temperatures (1400 ^{o}C) and furthermore, a significantly improved LOD could be

achieved for Os. In the common methodology of the ETV technique, vaporization temperatures greater than 2000 $^{\circ}$C are required for the introduction of the PGEs to the plasma.

The capability of ICP-MS for the determination of Pt in human urine and road dust samples was exploited by comparing the versatility of PN and ETV sample introduction techniques [43]. By dispensing 20 μl of sample aliquots into the ETV, an order of magnitude lower LOD was achieved compared to PN. UN, which improved the LOD for acidic standard solutions by a factor of 10, gave no improvement for the samples, even when using a desolvator/condenser unit for aerosols before transport to the ICP-MS. This was due to the enhanced aerosol output with a higher total salt concentration. Urine samples demand a dilution ratio of 1:10 for UN; otherwise, the interface between the ICP and the MS is clogged in a very short time.

Lüdke et al. [44] mounted graphite plates into an Anderson-type cascade impactor to collect diverse size-fractions of particles (0.35-16.5 µm cut-off diameter) originating from car exhaust fumes. The graphite plate, containing the sample, was subsequently inserted into an ETV unit for the simultaneous ICP-MS determination of Pt, Rh, Pd and Ir. If the sampled volume contained small amounts of particles, during the analysis of impaction target "discrete" signals originating from single particles were detected. In this case, based on Poisson statistics, one can calculate the number of particles from the relative standard deviation of the signal. Moreover, the mass of each analyte per particle can be calculated with the help of a calibration constant. The concentrations of the element pairs for both Pt-Rh and Pd-Ir exhibited good correlation with the PGE content of the catalytic converters of vehicles used for the period prior to sampling. It was deduced that Pt and Rh originated from the abrasion of catalytic converter material. On the other hand, Pt showed a poor correlation with

both Pd and Ir, indicating the origin of the latter two elements from other anthropogenic sources.

Spark ablation methods utilize a high voltage spark between the sample holder and the counter electrode to vaporize solid, electrically conducting samples. For example, Borisov et al. [46] analyzed the PGE content of various brands of catalytic converters using spark ablation sample introduction to the ICP-MS. For this purpose, the electrically non-conducting samples were mixed with graphite powder and pressed into pellets. The pellets were placed into the chamber of the spark ablation device, into which argon was passed to carry the released sample aerosols into the ICP-MS. These aerosols encompassed a very wide size distribution, including large particles, which caused the generation of signal spikes. Moreover, this interference was amplified when the spark wandered on the sample surface. To overcome this effect, it was necessary to use the spray chamber of the ICP-MS as a pneumatic buffer, which limited the size distribution of the aerosols routed into the ICP. This arrangement yielded a more stable signal, thus a more precise analysis. However, due to the background shift and its drift, as well as the "spark wandering", the attainable LOD in spark ablation was found to be higher, by about one order of magnitude, than that found with PN [45].

ETV sample introduction has definite advantages over conventional, nebulization-based sample introduction methods used for liquid/slurry samples: (1) higher sensitivity; (2) reduced extent of oxide formation; (3) decreased molecular ion formation; (4) tolerance for the analysis of samples with high acid and organic matrix content; (5) less probability of non-spectroscopic interferences via selective vaporization; (6) avoidance of plasma over-loading effects by solvents; (7) ability to analyze small sample volumes (some µl) and (8) ability to directly analyze solid

samples without any laborsome sample pre-treatment step. On the other hand, ETV methods have certain shortcomings stemming from graphite material used as vaporization surface; i.e., carbide formation, deterioration and memory effects, which can manifest as delayed and/or tailed transient peaks. When metal ETV is used, durability and reduced temperature range appears to be limitations [142]. The matrix-dependent volatility of analytes in ETVs can be overcome by proper choice of heating programs or addition of volatilization agents (e.g., Freon and PTFE powder) to the samples, the latter being very suitable for the evaporation of refractory elements [74]. For solid sample introduction ETV methods, the sample amount inserted into the vaporizer unit is restricted to 10 mg or less. Moreover, the homogenization of samples by micropulvarization and sieving is often a requirement, which diminish one benefit of direct solid sampling, i.e., the minimal sample preparation [142].

3.3.4. Laser ablation of solid samples

For the LA-ICP-MS measurement of PGEs in road sediments, Motelica-Heino et al. [42] applied ultraviolet (UV) and infrared (IR) lasers sampling of pressed pellets. An improved precision was achieved with the UV laser compared to that of the IR. Possible interferences for Pt and Rh were tracked by evaluating the isotopic pattern of the analytes, which matched well the natural abundance ratios, indicating no interference on these analytes, whereas Pd exhibited sensitivity to interferences.

Rauch et al. [62] performed spatially resolved analysis of PGEs on urban particles using a scanning LA-ICP-MS technique. The samples were placed in a quartz-topped cell. An optical system with a zoom of up to 800-fold was used to locate the position of the samples. A Nd:YAG laser beam was focused onto the surface of the particles which was scanned along a line with a controlled speed,

energy and spot-size. The generated ablation products were introduced directly to the ICP source. Focusing of the laser beam did not appear to be a problem because of the small difference between the particle sizes, and also a parallel beam was applied for verification. Elemental associations can be preferably determined with a small spot size, a low energy and a slow scanning speed [63]. By this method, the scanning of nanometer-sized particles is possible, an advantage also utilized for the determination of PGEs in the feathers of some raptor species and their prey [76]. These studies revealed predominantly small microparticles in the nm range deposited on the external of feathers.

Solid tree bark samples were probed by LA-ICP-MS to determine Pt and its dispersion as microparticles [31]. The laser beam was focused onto the sample surface separately at the start and end points and ablation was performed along the bark texture to minimize the effect of uneven/rough surface, which enabled establishment of the distribution of Pt on the barks. As a result, extremely non-homogeneous and highly dispersed Pt particles were found in the barks. By the detection of transient peaks, the associations of Pt with Pd and/or Rh were also revealed, which is important for the elucidation of the emission source. Tree barks are also efficient hosts for the accumulation of atmospheric aerosols and airborne particulate matter [30]. Consequently, they can be utilized as passive biomonitors for the assessment of the environmental impact of catalytic converters. In recent studies [31, 32], the barks of trees located close to motorways were used as natural "enrichment" substrates for the collection and pre-concentration of trace elements, including Pt. The analysis was completed either by LA-ICP-MS (as above) [31], or after digestion and dissolution of the samples by conventional (PN) ICP-MS methods [32]. Comparison between SF-ICP-MS and Q-ICP-MS analysis results revealed a fairly enhanced Pt concentration

for the latter technique, which was associated with the existence of possible interferences with this method [32]. However, the lack of HfO^+ interference and the close analytical results indicate that both methods can be well applied for the measurement of trace Pt in barks.

LA solid sample introduction methods offer the possibility of "scanning" sampling on the surface of the samples studied, the resulting information permitting construction of a "concentration map" of the bulk. For aerosol samples, it also makes possible the evaluation of the distribution of particles, which is important information from the viewpoint of assessment of PGEs on health.

3.3.5. Pre-concentration/matrix separation methods

Ultra-trace levels of PGEs accompanied by a high number of matrix constituents in environmental samples often requires pre-concentration and/or matrix separation procedures to be applied in connection with ICP-MS, to obtain accurate analytical results [117].

Akatsuka and McLaren [117-119] applied pre-concentration/separation techniques for the determination of Pt in environmental samples by ICP-MS. The strong binding ability of PGE chloro complexes to anion exchange resins in HCl solutions and the few number of other elements which form such anionic complexes provides an excellent basis for separation purposes [41, 59, 81, 118]. However, the elution of the strongly bounded Pt from the column is often a difficult task, even by the use of relatively high amounts of hot acids [59]. Additionally, the regeneration of the column, due to incomplete elution, requires successive cleaning procedures.

For the above reasons, there was a need to develop separation procedures which offer some advantage over the former methods. A good example is reverse

phase anion-exchange chromatography utilizing hydrophobic molecules with proper functional groups (e.g., C_{18} column coated with a quaternary ammonium salt) [117, 119]. Complete recovery of Pt was obtained with a mixture of relatively small volumes of HCl and $HClO_4$, whereas the main matrix components of airborne and geological samples, including the most important interferent Hf, were retained on the column [117]. A successful approach utilizes a 20-fold pre-concentration of Pt^{2+}, as its bis(carboxymethyl)-ditiocarbamate (CMDTC) complex, on hydrophobic XAD-4 resin and elution in the reverse direction by ethanol. This pre-concentration step also exhibited complete separation of most matrix elements, as well as removal of HfO^+ interference from all Pt isotopes [34].

Mukai et al. [80] elaborated on a rapid and sensitive FI-Q-ICP-MS method for Pt determination in airborne particulate matter. The FI-system consisted of a cation exchange column for the trapping of the major matrix components of the airborne particulate matter (e.g. Al, Ca, Fe, Na, etc.) and of Hf traces. This approach was applied to the quantitation of Pt and Ir in natural waters and sediments complemented with an ID method for calibration (see Section 3.4.) [81]. The cation exchange resins, applied in HCl solutions, retain the base elements of the samples, whereas they let the Pt pass through the column as its chloro complex. However, this methodology is generally applicable at $\mu g\ g^{-1}$ Pt levels, whereas for lower Pt concentrations the accuracy of the quantification is quite limited.

Hidalgo et al. [40] connected a FI system incorporating an alumina micro-column to the ICP-MS for the on-line pre-concentration and determination of Pt in natural waters. Pt was pre-concentrated on an activated alumina column at pH of 1.5-3.0, to prevent analyte breakthrough during the aspiration of the samples. Optimized volumes of ammonia solution were applied as an eluent, to obtain sharp transient

signals, a quantitative elution of Pt, a high pre-concentration factor, and minimum possible background contamination. The nominal pre-concentration factor was 300 for 5 min sampling time.

An efficient separation method for PGEs from biological matrices is cloud point extraction [83]. This procedure relies on the use of O,O-diethyl-dithiophosphate as a complex forming agent and Trition X-114 non-ionic surfactant. By increasing the temperature up to the so-called cloud point, a phase separation occurs, resulting in an aqueous phase and a surfactant-rich phase that containing the analyte complex. This separation method was utilized for ICP-MS determinations of five PGEs, but it proved to be inefficient for the pre-concentration of Ir.

3.4. Calibration and data evaluation

The application of proper calibration and evaluation in ICP-MS methods is important for attaining accurate analytical results. A typical ICP-MS evaluation method is isotope dilution (ID) [41], which requires the addition of the pure isotope of the analyte in a known amounts to calculate the total amount of analyte based on (measured) natural abundance ratios. This method however, has potential limitations due to differences in matrix effects caused by isotopes having possibly diverse chemical specifications. Therefore, it can only be utilized with proper matrix homogenization and spike equilibration. However, to assess an optimally low accumulation and propagation of errors for the total analytical procedure, due to the increased number of analytical operations, some general principles of this method have to be followed [65].

Mathematical correction procedures have been extensively applied for the evaluation of the PGE content of environmental samples. The prerequisite for the

applicability of these methods is the linear dependence of the interferent signal on the analyte concentration. In catalytic converter samples, the HfO^+/Hf^+ ratio was applied for the mathematical correction of the HfO^+ interference, an approach which proved to be less accurate than chemical separation with ID [35]. For the sample solutions, the ZrO^+/Zr^+ ratio was measured and used in the correction formula to bridge any possible shift in the Hf molecular/element ratios with changes in the matrix composition and/or operating conditions, and even by the aging of the interface. A similar correction method was also applied for the correction of $^{179}Hf^{16}O^+$ (on ^{195}Pt), $^{40}Ar^{65}Cu^+$ and $^{89}Y^{16}O^+$ (on ^{105}Pd), and $^{40}Ar^{63}Cu^+$, $^{87}Rb^{16}O^+$, $^{87}Sr^{16}O^+$ and $^{206}Pb^{2+}$ (on ^{103}Rh) interferences on the Q-ICP-MS determination of Pd, Pt and Rh in car exhaust fumes [36] and in a freshwater isopod [77]. In the latter work, the signal ratios were tracked and applied for the correction of the effects of Hf, Cu, Y, Rb, Sr, and Pb interferents. One of the internal standards, ^{191}Ir, was utilized for the determination of Pt, Hf and Pb, whereas the other, ^{115}In, was employed for Pd, Rh, Cu, Y, Rb and Sr measurements [77]. For the determination of Rh in urine, Krachler et al. [27] evaluated the influence of $^{206}Pb^{2+}$ on ^{103}Rh based on the counts at mass 103.5 corresponding to $^{207}Pb^{2+}$, and on the abundance ratio of ^{207}Pb and ^{206}Pb. This monitoring method indicated the necessity of mathematical correction. However, the method could not be used for analysis of environmental samples, because of the presence of serious interferences by the high concentration of matrix salts. Similar results have been achieved in other work [29], in which the Pt and Rh contents of the aerosol samples could be, in general, adequately evaluated by using a mathematical correction method. However, the Pd content in this determination was interfered with the high Cu and Y content of the samples [29]. For the analysis of ice and snow

samples [6], the effect of Cd was corrected by monitoring the Cd content of the samples and subtraction of the contributing concentration from the ^{106}Pd signal.

Employment of internal standards is a popular ICP-MS evaluation method which involves the addition of a standard element of known concentration to the samples; the intensities of this element are then used as a reference to calculate the unknown concentration of the analytes. In some cases, it is subject to isobaric interferences from some matrix components (e.g., In internal standard was interfered with Sn and Cd content of road dust [64]). The internal standard method with the use of Ir was proved to be not fully quantitative [34]. Therefore, ID could also be applied for calibration together with the employment of FI for sample introduction [34].

Motelica-Heino et al. [42] used laboratory reference materials (LRMs) for calibration purposes; i.e., a matrix was prepared from road sediments collected in 1984, and was applied in two different calibration methods: first, the addition of spikes to a nominally pure matrix material and second, PGEs were added in solid form by mixing certified reference materials (CRMs) with the matrix, i.e., producing LRMs. The best quantification strategy was the standard addition of PGEs to the road sediment samples.

For a long time, only three CRMs were available with certified PGE content, two of them based on ore matrices (nickel sulfide and nickel-copper-cobalt) [123], one as a recycled monolith catalytic converter in powder form (NIST SRM 2557 with Pt, Pd and Rh contents of 1.13, 2.33 and 0.135 mg g^{-1}) [29]. The nature of these matrices together with their high PGE levels differ from that of in various environmental compartments (e.g., road dust, airborne particulate matter, etc.) which makes them not very suitable for the quality control of environmental samples. In order to enhance reliability of the quantification of PGEs in environmental matrices, a

roadside dust CRM (BCR-723, IRMM Institute for Reference Materials and Measurements, Geel, Belgium) was recently certified with Pt, Pd and Rh contents of 81.3, 6.0 and 12.8 ng g^{-1}, respectively [145]. The inter-laboratory study was accomplished using mainly ICP-MS techniques with ID, whilst for comparison, GFAAS, TXRF, RNAA, and ASV methods were also applied [82, 123].

It can be concluded that the proper calibration of ICP-MS methods for the determination of PGEs very often appears to be difficult, because of the complexity of the matrices, which give rise to interferences. In general, the application of two diverse calibration procedures, as above, can be recommended for the quantification of PGEs in "difficult" environmental and biological materials.

4. GFAAS and ICP-AES methods

4.1. General

In GFAAS analysis, usually a small volume (typically 20 μl) of the sample solution, or solid sample (0.1-1.0 mg) is dispensed into a graphite atomizer mounted in the optical path of an absorption spectrometer. The sample is pretreated (dried, pyrolyzed) for the removal of the matrix constituents, and then atomized (electrothermal heating) to produce free atomic vapour of the analyte. Graphite atomizers provide nearly a 100 to 1000-fold increase in the residence time of the sample vapors in the optical path compared to flame and ICP excitation-atomization sources. Certainly, a lower dilution of the sample vapor prevails for the analyte, as well as for the matrix constituents, which entails greater gas-phase (chemical) interferences [74]. Additionally, the accessible calibration range is usually not wide enough to cover the required concentration values occurring in environmental/biological samples. Although GFAAS is usually referred as a single

element technique, the most up-to-date instruments possess the simultaneous, multi-element capability for up to six analytes [112, 113].

ICP-AES methods are characterized by lower sensitivity to non-spectral (chemical) interferences (i.e., more robustness), but the large number of transition metals present as main constituents in environmental matrices can cause spectral interferences with the determination of PGEs. These effects however, can be successfully overcome by the selection of alternative analytical lines, and/or matrix separation. ICP-AES methods also possess the possibility for simultaneous measurement of PGEs.

4.2. Interference effects and their elimination

The GFAAS determination of PGEs, as can be deduced from ETV studies noted above, requires high atomization temperatures due to the high vaporization temperature of the PGE compounds. It is to be noted here that for small sample amounts, i.e., below the μg range, the vaporization of the sample constituents takes place around their melting points. Several matrix constituents, especially chloride salts of transition metals, have been reported to cause interference effects with GFAAS measurements [54].

Generally, the most robust, commercially available GFAAS instruments offer the possibilities of stabilized temperature platform furnace (STPF) conditions [94] and Zeeman-effect background correction in connection with a transversely heated graphite atomizer (THGA). GFAAS systems, based on this concept, provide higher and more homogeneous temperature conditions in the atom reservoir for the vaporization/atomization of PGEs, and a less intensive extent of interferences. These conditions also imply some two orders of magnitude linearity of the calibration,

which is a necessary compromise for solving the analytical problems using instrumentation having lower maintenance costs as compared to ICP-MS.

With the aim of the GFAAS analysis of Pt in car exhaust fumes, the matrix effect from excess concentrations of Si, S, Zn, P, Fe, Ca, Pb and Al on the Pt signal was studied in HNO_3 medium [54]. The HCl, HNO_3, and H_2SO_4 solutions applied in the 1-10 mol l^{-1} concentration range had no effect on the Pt signal, but aqua regia at higher concentrations resulted in signal suppression. The Zn, Ca, and Pb matrices caused a slight signal decrease at $1:10^5$ excess ratios to Pt, whereas P slightly amplified the Pt signal. At higher analyte-to-matrix ratios ($1:10^6$), both Al and Si suppressed the Pt signal. Several transition metals (e.g., Co, Cu, Fe and Ni, applied in chloride, or nitrate forms) have also been reported, even at excess ratios as low as 100-fold, to interfere with the GFAAS determination of Rh to a very diverse extent [78]. Certainly, the effects of chloride salts have been emphasized more, according to the GFAAS literature [84].

It is noted here that the chemicals involved in the pre-concentration/separation procedures for PGEs could interfere with their GFAAS determination. For example, KSCN complexing agent was found to cast a high non-specific absorption on the AAS signals of Pd and Pt; this drawback did not appear for glycine and thiourea [95]. The increased concentration of eluents, like HCl and NH_3, in the sample solutions arising from ion-chromatographic separation can also cause a decrease of in the Pt signal in subsequent GFAAS determinations by 20 and 30 %, respectively [96]. At 1.2 mol l^{-1}, thiourea increased the Pd signal by some 10 % [95]. In the presence of thiourea, the Pt transient signals developed higher appearance and peak maximum times, corresponding to a higher vaporization/atomization temperature, which was attributed to the formation of less volatile, PtS-type compounds [96].

Optimal graphite furnace vaporization-atomization conditions for Pt were studied by graphite furnace electrothermal atomization laser excited atomic fluorescence (GF-ETA-LEAFS) using a Cu vapor laser pumped dye [86]. This high repetition rate dye laser probes the free Pt atoms in the graphite furnace more efficiently than the usual radiation sources (i.e., hollow cathode, and electrodeless discharge lamps). Thus, the former source exhibited an exceptionally low LOD (50 fg). When proper pre-atomization steps are used, the spectrum from the blanks (Pt-free matrix solutions) did not show any fluorescence bands of molecular origin. This means that the method is free of molecular interferences which, otherwise, demand efficient background correction in GFAAS. Comparison of the capability of the pyrolytic graphite L'vov-platform, the Katskov-type graphite filter, and conventional wall atomization resulted in a preference for the latter, because it exhibited a lower atomization temperature. Generally, these "graphite" probe techniques have drawbacks for the vaporization-atomization of refractory elements, emerging from two combined effects: (1) their thermal inertia and the temperature gradients they induce inside the furnace, and (2) the increased probability of carbide formation due to the slow release/evaporation of the sample from the probe. To overcome the latter drawback, L'vov and Pelieva [114] proposed use of a Ta-lined furnace with Ta-platform. Although PGEs are not carbide-forming elements, the vaporization of Os in the form of its low-volatility oxides can be more efficient from a metal probe surface, like the Ta-platform, because of the lower probability of the Os compounds being reduced to the rather refractory metal (see Section 3.3.3.).

4.3. Pre-concentration and matrix separation methods

As was aforementioned, the ultra-trace levels of PGEs in environmental samples requires pre-concentration of the analytes, and/or separation of the matrix for their detection by GFAAS and ICP-AES. For example, Patel et al. [26] used Sn(II) chloride and N-butylacetamide as complexing agents for the separation and enrichment of Pd in soil samples. This method was based on the formation of Pd(II)-$SnCl_3^-$-N-acetamide complex and its liquid-liquid extraction with 1-pentanol, followed by the GFAAS measurement.

Cantarero et al. [49] used FI pre-concentration of Pt on an alumina micro-column prior to its GFAAS determination, which resulted in an enrichment factor of 30 for natural water samples. Moreover, a decreased analysis time was achieved with a LOD of 0.33 $\mu g \; l^{-1}$ in tap water samples. From the possible interferents on the pre-concentration process, 1 $g \; l^{-1}$ Cl, applied as NaCl, caused a significant decrease in the retention of Pt, moreover, stronger effects of Br and I have also been noted.

Godlewska-Żyłkiewicz et al. [95] applied a Cellex-T resin for the pre-concentration and GFAAS determination of Pd and Pt in tap water and in catalytic converters. Glycine, thiourea and KSCN were utilized as suitable complexing agents for the elution of Pt and Pd from the microcolumn. Glycine was found to be the most successful agent for the separation of Pt and Pd, since it forms complexes of diverse charges with these elements. In other work, the efficiency of three different sorbents (alumina, silica gel and Cellex-T) was compared for pre-concentration of Pt from water samples [96]. For activated alumina packed column, the best elution was achieved in NH_3 solution, yielding a 400-fold pre-concentration, which is a significant improvement compared to former results [49]. A 100 μl volume of 10 % thiourea completely eluted Pt from a modified silica gel loaded column. For a Cellex-T filled column, thiourea was the best with an enrichment factor of 133. The latter resin

possessed the highest break-through capacity; therefore, it could be useful for the analysis of environmental matrices. Similar anion-exchange methods were developed for Rh, using Cellex T resin with EDTA complexation [78].

Vlašánkova et al. [53] applied a modified silicagel (C_{18}) for the separation and pre-concentration of PGEs as ion association (pairing) complexes with the cation of the onium salt of N-(1-carbaethoxypentadecyl)-trymethyl ammonium bromide, prior to ICP-AES and ICP-MS determinations. The sorption recovery was 100% for Pd and Pt, 90% for Os, and 85% for Ir. On the other hand, very poor recoveries were established for Ru and Rh, i.e., 4 and 8%, respectively, making this sorption method unsuitable for these two PGEs.

A fully automated on-line pre-concentration of Pd was accomplished on a micro-column loaded with the strong complex forming agent N,N-diethyl-N'-benzoylthiourea (DEBT) [55]. The Pd complex was eluted with 60 μl ethanol and directly transferred to the graphite platform for GFAAS determination. From a 5 ml sample solution, a 200-fold sensitivity enhancement was achieved, with a LOD of 13 ng l^{-1}. In 6.5% (v/v) HNO_3 solutions, alkaline, alkaline-earth, and transition metals, such as Cd, Co, Cu, Fe, and Ni, etc., were tolerated up to 10 g l^{-1} concentrations. The authors found coupling with the GFAAS method more rugged than those with laser absorption fluorescence spectrometry (LAFS), ICP-MS, or INAA. Although the latter techniques result in a lower LOD, they necessitate more expenditure of work and modification of the pre-concentration method [131]. A similar coupled GFAAS method was applied to the determination of Pd in road dust [16, 137] and urban aerosol samples [137]. For pre-concentration purposes, DEBT complexing agent was also applied to bind Pd on a C_{18} micro-column.

Lee et al. [56] also applied on-line pre-concentration of Pt, Pd and Rh as bis(carboxymethyl)-dithiocarbamate (CMDTC) complexes on an XAD-4 filled microcolumn after the off-line addition of solid CMDTC to the sample solution containing $SnCl_2$ and HCl. The sample solution was segmented in the pre-concentration unit by air in order to prevent dispersion. The eluate was collected on-line in a PTFE loop and was forced either into the graphite furnace by nitrogen, or into the ICP by the use of a carrier solution. The pH of sample solutions, the concentration of the complexing and reducing agents, and the flow rate in the column were also studied and optimized.

Hodge et al. [59] determined Pt and Ir in marine samples at pg levels. The analytes were isolated in their anionic forms on AG1X2 (for Pt) and AG1X8 resin (for Ir) with subsequent purification by uptake on a single ion-exchange bead (IRA-900) and GFAAS detection. Stripping of the Pt from the bead with HCl/thiourea and injection of this solution into the graphite furnace was preferred over direct insertion, or wet digestion of the bead. Although this procedure proved to be very sensitive with an absolute LOD of 15 and 20 pg for Pt and Ir, respectively, it was handicapped by the laborsome dissolution and pre-concentration procedures. Polystyrene based sorbent with DETA (cross-linked polystyrene with diethilenetriammine groups) complex forming groups was also efficiently utilized for the pre-concentration of all six PGEs [52].

Komárek et al. [50] proposed the adsorptive accumulation and electrodeposition of Pd and Pt onto the internal surface of a pyrolytically coated graphite tube, which subsequently served as an atomization surface for GFAAS measurements. For this purpose, a flow-through cell was used for introducing the sample solution into the graphite tube, for supporting the deposition of the sample

aliquot at the middle part of the tube. The sample position has a significant importance for end-heated tubes which, compared to the side-heated designs, have an inhomogeneous temperature distribution along the longitudinal axis. Generally, for the former atomizers, the preferred atomization site is the middle of the furnace. This region can reach the nominal preset atomization temperature. The sensitivities, which depended on the flow-rate and sample volume applied in the "deposition" cell, were essentially the same for the two different enrichment techniques: i.e., 8-24 times higher for Pd and Pt than with the standard deposition of 20 μl sample aliquots. Similar electrodeposition methods were employed for Pt [51, 98], Pd, Rh and Ru [98] in dust samples prior to their GFAAS determination.

Pre-concentration of Pd from tap water and road dust samples on a graphite electrode was performed in a flow-through electrochemical cell at a controlled potential [97] prior to their GFAAS determination. After pre-concentration of Pd, the polarization of the electrodes was changed and the deposited metal was dissolved with the assistance of a proper stripping agent.

LAFS equipped with GF-ETA atomization source and GFAAS were applied to the determination of Pd in airborne particulate matter [58]. The pre-concentration procedure was similar to that employed in Ref. [55]. Using this enrichment technique combined with ETA and LAFS detection, a very enhanced detection power was achieved with an LOD value as low as 2 ng l^{-1}, which was lower by around one order of magnitude than the corresponding GFAAS value [58].

5. Voltammetry

Early ASV methods involve the masking of sulphide or thiourea peak by Pt, and the deposition of Pt on graphite, or glassy carbon electrodes from solutions of

$PtCl_4^{2-}$, or $PtCl_6^{2-}$ prior to voltammetric determination [109, 110]. A LOD of lower than 2 µg/l is difficult to achieve by these methods, thus they are not sensitive enough to meet the demands of PGE determination in environmental/biological matrices.

An ultra-sensitive ASV determination of Pt is possible by the utilization of a catalytic hydrogen wave [66, 103-108, 121, 122]. The method is based on the potential supported accumulation of the Pt^{II} complex (a condensation product of formaldehyde and hydrazine, called "formazone") at the surface of a hanging mercury drop electrode. The electrochemically active complex lowered the hydrogen overpotential at the mercury electrode and produced a very sensitive catalytic current, which could be measured in the differential pulse mode [103, 104]. This analytical procedure exhibits an absolute LOD of 0.5 pg for simple acidic solutions, but can be noticeably enhanced in the presence of matrices.

The method is extremely sensitive to the presence of organic matrix constituents. For example, in blood analysis, the presence of surface-active components initiated a highly enhanced background. Hence, for the analysis of PGEs in matrices of organic content, the complete decomposition/removal of the organic constituents is required. Moreover, an important aspect of ASV 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 [66]. Similar ASV methods were also applied for the analysis of Pt and Rh in grass samples [67] and spruce shoots [100]. Other research teams also applied this ASV method to determine Pt in a variety of environmental and biological samples, such as airborne dust [105, 106], plants [105], tissues [105], body fluids [107] and seawater [108]. Some authors [105] reported memory effects and pointed to

the inefficiency of three-step cleaning procedures [57] for the elimination of carry-over with samples of fairly high Pt content [105].

Measurement of Pd by electrochemical methods is rather difficult due to mainly the irreversibility of the electrode processes [149]. Polarographic and related techniques have shown that the reduction of Pd becomes faster (easier) in complex forming media. Further increase of the sensitivity and selectivity of ASV and other advanced electroanalytical techniques can be achieved by the modification of the electrode and/or an enhanced adsorption of reactants. Ligands containing oxime groups, well known from their use in gravimetric analysis, are often used for the adsorptive accumulation of Pd on Hg electrodes. Wand and Varughese [150] elaborated a very sensitive ASV method based on the pre-concentration of Pd-dimethylglyoxime complex on a hanging Hg electrode, which is a promising approach for the determination of ultra-trace Pd levels, as permitting a LOD of 20 ng l^{-1}. In another study, the optimization of the critical parameter of this method (i.e., ionic strength, electrode area, pre-concentration time, transport rate to the electrode and potential scan rate) and its feasibility for the determination of Pd in some spiked biological samples (i.e., mushroom, beebread, flour) were reported [149].

In general, the above electroanalytical methods have several advantages over ICP-MS for the routine analysis of some PGEs in biological matrices, such as the lower LODs (nearly 100-times for Rh [67]), which provide assessment of both exposed and baseline PGE levels. Further advantage is the lower operating costs than ICP-MS, and the small sample volume required for the analysis, but they are handicapped by the laborsome sample preparation steps (e.g., the mandatory de-aeration), their poorer robustness, and usually, their single element nature.

6. X-ray spectrometry

X-ray absorption and fluorescence spectrometric methods are generally not directly suitable for the determination of ultra-trace concentrations of PGEs in environmental matrices. For example, wavelength dispersive X-ray fluorescence (WDXRF) methods are only applied to the quantitation of PGEs from catalytic converter units possessing a relatively high precious metal content [45, 46], and with appropriate evaluation procedures (e.g., fundamental parameter method) for the analysis of blood samples with enhanced Pt content [99]. On the other hand, total reflection X-ray fluorescence (TXRF) methods have been recently developed for the determination of Pd in urine samples of exposed and unexposed persons and, in some environmental samples, such as poplar roots, airborne particles [87] and road dust [87, 88] and in various tissues of exposed eels [88]. One method utilized the co-precipitation and collection of Pd on a Hg droplet which was transferred to the sample carrier (target) of the TXRF instrument. The Hg was then completely evaporated by the assistance of a Hg absorber, and the remaining dry residue, containing the Pd traces, was analyzed. This combined pre-concentration/separation method resulted in an absolute LOD of below 35 pg [88].

It is to be noted here that X-ray photoelectron-spectroscopy could be successfully applied to the analysis of microparticles from the catalytic converters [128]. The PGE particles were found to be attached to larger particles of the base material (Al_2O_3) also released from the catalytic converter.

7. Nuclear and radioanalytical methods

Instrumental neutron activation analysis (INAA) methods have also been elaborated and applied for the determination of PGE traces in environmental and

biological matrices [15, 69, 70, 71]. These methods involve the irradiation of samples by gamma-rays and subsequent measurement of the activated analyte "indicator" nuclide. The interference-free determination of [190]Pt gamma-peak at 538.9 keV suffers from low sensitivity for most environmental and biological samples [69] due to the low natural abundance (0.01 %) of [190]Pt. The measurement of [199]Pt is limited by its short half-life of 30.8 min. Consequently, Pt is often determined via [197]Pt, or via the [199]Au daughter of [199]Pt [69]. However, in a variety of environmental and biological samples, [24]Na interference with the [197]Pt permits analysis only after long decay times. The [197]Pt also suffers from the [197]Hg interference. In order to overcome the above drawbacks, Alfassi et al. [69] determined Pt in aerosol samples by a rapid INAA method based on a mathematical correction for the interference of [47]Sc (daughter of [47]Ca) on the Pt indicator nuclide [199]Au. In principle, the contribution of Pt and Ca signals (at the 157-161 keV peak) can be separated to its components either by calculating the signals of [47]Sc from the signals of its parent [47]Ca, or by making use of the differing half-lives. Because of the diverse half-lives of [199]Pt and [47]Ca, the formation and decay of [199]Au and [47]Sc have a different temporal dependence [69]. Later, this method was successfully utilized for the determination of Pt in aerosol samples [70].

Radioanalytical neutron activation analysis (RNAA) methods also utilized the detection of [199]Au indicator radionuclide [111]. The separation of Au was performed on polyurethane foam from 1M HCl. The presence of Sb at concentrations higher than 5 μg g^{-1} interfered with the determination; thus, further decontamination of the indicator radionuclide fraction was necessary. This method exhibited a LOD at ng g^{-1} Pt levels. The second-order interfering reaction from Au can strongly influence the LOD and the accuracy. The LOD of Pt depends on the Au/Pt ratio in the sample,

which determines the optimum irradiation conditions (i.e. neutron flux and irradiation time) [111].

Heinrich et al. [71] applied INAA with fire-assay for the pre-concentration and determination of Pd, Pt, and Rh deposited in soils nearby motorways. The thermal neutron irradiation of the samples was performed in two cycles, i.e., a short-term cycle for Pd and Rh, and a long-term cycle for Pt. By this technique, Pd was determined via ^{109}Pd and Pt via ^{199}Au. The extent of Au-interference was negligibly small, due to the low Au-content of the samples (1-3 %) compared to the Pt concentration. Similarly, the other PGEs, as well as Au and Re, can be detected simultaneously after a long-term irradiation cycle via the activated products of ^{192}Ir, ^{191}Os, ^{103}Ru, ^{198}Au, ^{188}Re and ^{186}Re [71].

These sensitive techniques offer very low LODs (ppt levels), but their low sample throughput and the need for a radiation source to produce activated species of the samples restrict their accessibility for common analytical laboratories.

8. Speciation studies

Throughout this section, the term "speciation" is used in a broader sense, as most of the studies focused on the characterization of those molecular fractions of the matrices to which the PGE species are bound, rather than on the identification of the binding forms of PGEs.

PGEs are typical transition metals, which preferably react with diverse kinetics to form various complex compounds [8]. Cleavage of these coordination bonds takes place more easily than with covalent bonds. For example, Pt compounds often show fast species transformation in solutions [93] as well as in various environmental compartments [72]. Therefore, mild, non-alternating conditions and

fast analysis times are a prerequisite for speciation studies of these elements. The above conditions can be provided by those analytical separation methods which utilize either purely the physical features (e.g., size exclusion), or feeble chemical interactions (e.g., weak ion-exchangers) of the species for separation purposes.

Wei and Morrison [129] applied a sequential chemical extraction of gully pot (catch basin) sediment samples with ASV detection for the speciation of Pt. With this separation scheme, a distinction could be drawn between (1) exchangeable (by sodium acetate); (2) carbonate; (3) Fe and Mn hydrous oxide; (4) organic; and (5) residual fractions of the samples.

High performance liquid chromatography (HPLC) [72] and capillary electrophoresis (CE) [72, 124, 127] could be hyphenated with ICP-MS for the speciation of Pt in soils [72, 124, 127] and tunnel dust [124, 127]. The Pt-treated clay-like humic soil was extracted by an aqueous solution, which was analyzed for various Pt species [72]. In the HPLC technique, the stabilization of Pt-species (chloro compounds) by chloride addition was necessary to prevent their rapid hydrolysis to a variety of aqua-chloro complexes. However, the CE method showed a higher resolution power for the Pt-species, and its hyphenation to ICP-MS was utilized for the analysis of environmental and clinical samples [125, 126]. An additional advantage of the method is that it is not hampered by interferences [72]. On the other hand, HPLC hyphenation had a LOD of 25 ng l^{-1} i.e., 40-times lower than for CE hyphenation due to the higher sample intake of the former technique. By the use of the HPLC method, one cannot draw a distinction between the chemically very similar species, such as Pt-hydroxo- or chloro-compounds, but a differentiation is possible between the polar, mostly inorganic Pt-compounds and Pt-species with organic ligands. The CE hyphenation to ICP-MS could be advantageously realized by a home-

made "modified" Meinhard nebulizer [130]. This interface permits the suction flow from the nebulizer to be minimized, which is a mandatory prerequisite for on-line coupling.

The earliest results on the separation of Pt species from grass date back to 1994 [89, 90]. The authors isolated one main Pt binding protein of 180-195 kDa from "native" grass samples. In grass treated with Pt (uptake exclusively by the roots), this fraction of high molecular weight species increased and seven additional species were detected in the 19-1000 kDa range. In contrast to the native grass however, most of the adsorbed Pt (>90 %) was observed in the low molecular weight range [89]. The study of low molecular weight species (<1500 Da) in grass revealed that the Pt binding ligands can be characterized as partly oxidized oligosaccharides (about 2-5 monomeric units of aldonic, aldaric, or uronic acids). The origin of these species was attributed to the hydrolysis of biopolymers, such as pectin (polygalacturonic acid) [91]. In the latter work, Alt et al. [91] used ultra-filtration, gel-chromatography, and preparative isotachophoresis and a further separation by liquid chromatography with UV and pulsed amperometric detection to the low molecular weight species, whereas Pt was determined by a very sensitive voltammetric method. It follows from the above studies that the low molecular weight Pt fraction plays a more important role in the transformation and bioavailability of Pt, of which detection was also the purpose of the work below.

Klueppel et al. [92] studied Pt metabolites in cultivated grass treated with aqueous Pt solutions, and also in model experiments studying the binding capabilities of methionine, cysteine, and glutathione to Pt. For this purpose, the multi-element capabilities of ICP-MS were exploited with an on-line coupled size-exclusion chromatography (SEC) unit. This tandem technique offers the possibility of obtaining

on-line information on the metabolization of Pt (without any isolation of the species) by establishing correlation with other elements that co-elute with Pt. Moreover, the chemical interactions between the separation medium and the sample were successfully minimalized. The analysis of the low molecular mass components (<10 kDa) revealed five well distinguishable Pt fractions, for which the binding properties of Pt could be drawn from the multi-element monitoring of some possible partners (C, S, Ca and Pb). The drawback of the SEC is its relatively poor resolution, which is manifested in the composition of the fractions representing the mixtures of diverse species, not the pure compounds. By using additional columns, one can extend the resolution of SEC. Alternative separation techniques, such as the reversed-phase chromatography and anion-exchange chromatography, can also be successful.

Two-dimensional flatbed electrophoresis (FBE), encompassing two diverse separation schemes, namely isoelectric focusing (ISF) and polyacrylamide gel electrophoresis (PAGE), was combined with SF-ICP-MS for the speciation of Pt in human [101] and rabbit serum samples [101, 102]. Detection of the proteins was achieved via Ag staining, whereas for the Pt-carrying proteins, autoradiography (incubation of the samples with radiotracers) was applied with the assistance of laser densitometry. The gel was Ag stained, then analyzed, and the matching with radiotracer measurements was confirmed by an imaging densitometer. The drawback of the FBE technique is that application of the electric field causes the release of high amounts of Pt that can exceed the amount of Pt present in the samples [126]. On the other hand, no Pt-release was detected with the CE technique [126]. The above results necessitate the replacement of Pt electrodes with Au for studying Pt species with the FBE method. Additional advantage of the CE technique is that it permits the coupling

of the ICP-MS "on-line", whereas with FBE it is possible only "off-line". A detailed review of the CE techniques of PGEs has recently been published [115].

Pulsed amperometric detection enables the selective determination of metal-binding to carbohydrates in plant extracts, which was used for the analysis of small volumes of HPLC fractions [132-134]. The selectivity is primarily a function of the catalytic surface state of the working electrode and not solely the redox potential of the analyte [132]. Cyclic voltammetric detection of the Pt-species was also applicable, but only for making a distinction between compounds of diverse functional groups, not a real identification of the single Pt-species [133, 134].

Speciation of anthropogenic PGEs demands highly sophisticated methodology due to the very low concentration of these elements in the environmental compartments, and the restrictions due to the fast species alterations. Nevertheless, this multi-disciplinary field of chemistry shows a rising trend, because of the increasing interest in the understanding of the transformation and bioavailability of PGEs in diverse biological matrices and environmental compartments.

9. Conclusions

Due to the continuously intensifying anthropogenic emission of PGEs, interest in their determination in various environmental and biological matrices has gained increasing attention. Likewise, the various forms of PGE compounds tend to readily undergo transformations under the very changing conditions of the various environmental compartments, as well as during the sampling and sample pre-treatment processes prior to their determination. These features demand high sensitivity, selectivity, and fast analytical methods, particularly for the recognition and quantitative determination of the exact binding forms of PGEs. For the latter

purposes, some electroanalytical techniques, such as ASV and cyclic voltammetry, have definite advantage over chromatographic procedures. Nevertheless, efficient separation and assignation of the various forms of PGEs always demands complementary use of these techniques. The trends in this particular field show that the speciation of PGEs in various environmental compartments and biological matrices will probably achieve a growing relevance.

Amongst spectrochemical methods, ICP-MS is found to be the most popular and robust technique for the determination of ultra-traces of PGEs in diverse environmental and biological matrices. Despite the high sensitivity, ICP-MS requires appropriate choice of sample introduction method, preferably one possessing the option of solid sample introduction. An alternative route to get rid of spectral and non-spectral interference effects is the application of prior matrix separation, which is frequently a pre-requirement for the accurate and precise determination of PGE ultra-traces by ICP-MS. It is to be noted that alternative (e.g. He) or mixed (e.g. $Ar+N_2$) plasma gases have a potential for the reduction of spectral overlap problems in ICP-MS [144], a possibility which has not yet been utilized to the determination of PGEs. The multi-element capability of ICP-MS offers the possibility of obtaining information on the possible binding partners of PGEs "on-line", consequently, the isolation of PGE species is not always necessary.

A variety of other sensitive methods, like GFAAS, INAA, TXRF and ASV, make it possible to perform complementary measurements in matrices often referred to as "difficult". This approach is of paramount importance in view of the lack of proper certified reference materials for several environmental compartments exposed to PGE emission by automotive catalytic converters. This latter consideration is valid for almost all of the matrices studied for the assessment of anthropogenic PGEs,

which suggests future tasks for analytical chemists. In the future, due to the continuously increasing PGE levels in the environment, the application of less sensitive analytical techniques (such as GFAAS, ICP-AES and TXRF) can become prevailing in this particular field of analytical chemistry.

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