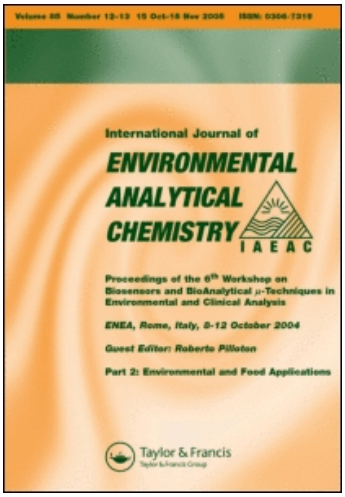


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# Comparison of open digestion methods and selection of internal standards for the determination of Rh, Pd and Pt in plant samples by ICP-MS

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# Comparison of open digestion methods and selection of internal standards for the determination of Rh, Pd and Pt in plant samples by ICP-MS

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An analytical procedure for the reliable determination of Pd, Pt and Rh in plant samples by inductively coupled plasma-mass spectrometry (ICP-MS) was developed. An ultrasonic nebulizer (USN) was used for sample introduction to improve sensitivity. Under various synthetic plant sample matrix compositions, it was established experimentally that moderate amounts (0.2–2%) of dissolved solids decreased the analyte signals significantly. Internal standardisation with In (for Pd and Rh) and Ir (for Pt) proved to be essential for obtaining correct results. Five open digestion approaches, used for converting solid plant samples to aqueous solution, were also tested for the purpose, namely dry-ashing, dry-ashing followed by HF attack, wet digestion with $H_2O_2$–$HNO_3$, wet digestion followed by HF attack and aqua regia digestion. Recovery tests in two spiked plant materials showed that only wet digestions must be used. With these ways, all PGEs could be reliably quantified by USN-ICP-MS without applying a separation or preconcentration step with a good precision (below 10% RSD). The aqua regia procedure was applied to the determination of PGEs in various plant matrices collected along a highway. Results showed that mosses were probably the best choice of samples to monitor the bioaccumulation of PGEs in time.

**Keywords:** inductively coupled plasma mass spectrometry ICP-MS; palladium; platinum; rhodium; plant sample



## 1. Introduction

The concentration level of platinum group elements (PGE) is normally very low in the nature [1]. However, anthropogenic emissions of Pd, Pt and Rh into the environment have significantly increased since the last decade [2,3]. These elements are especially used in automobile catalytic converters to reduce the emission of carbon monoxide, nitrogen oxides and hydrocarbons [4]. The abrasion of these catalytic converters forms airborne particulate matter which deposits on roadside surfaces and soils. It results in a bioaccumulation of PGE in living organisms [5]. The monitoring of PGE, therefore, has

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importance with respect to the estimation of the future risks to human health and to ecosystems. Several PGE salts (Pd and Pt chlorides) have been reported as causing asthma, allergy and other serious health risks to humans [2,6].

Analysis of plant samples is certainly a good way of judging the bioavailability of emitted PGE under natural conditions [7]. Plant species uptake metals efficiently from the soil and are often employed as bio-indicators for environmental pollutions. Several authors have discussed the methods for the determination of PGEs in the environment [8–13]. Accurate determination requires analytical instruments with high sensitivity (detection limits below $10\,ng\,g^{-1}$) and the control of interferences [14]. Accurate determination also requires an efficient digestion method for plant materials.

Inductively coupled plasma mass spectrometry (ICP-MS) is the most promising technique for the determination of ultra-trace levels of elements in environmental samples. ICP-MS is often used for the determination of PGE [15]. However, the performances of an ICP-MS instrument with quadrupole are sometimes only just acceptable for PGE measurements. The very high sensitivity of inductively coupled plasma sector field mass spectrometry has been used by some workers [13,15–16]. However, these spectrometers are very expensive and must be used carefully. Other methods require additional separation and preconcentration steps prior the determination of the analytes [14,17–19]. These procedures are time consuming, prone to either loss of analytes or contamination of samples and are unsuitable for multi-element analysis. The main limitation in the detection power is the low sample introduction efficiency with a pneumatic nebulizer. Coupling an ultrasonic nebulizer (USN) to an ICP-MS spectrometer may lead to an improved performance [20].



Nevertheless, the ICP-MS technique is sometimes plagued by isobaric interferences concerning PGE [8,11,14]. In many cases, spectroscopic interferences can be avoided by choosing alternative isotopes. ICP-MS is also subject to non-spectral interferences. Non-spectral interferences induced by high concentrations of matrix constituents generally manifest by suppression of the analyte signals [21,22]. A significant analytical error can result for samples with relatively high matrix composition such as mineralised plant solutions.

Another crucial step in the analysis of PGE is sample digestion and the complete dissolution of analytes. Acid dissolution procedures are the most popular methods used for metal determinations in plant materials [23]. The low reactivity of PGE, their numerous oxidation states, their ability to form many species in a given oxidation state make determination, especially at low concentration levels, very difficult [18,24]. The sample preparation methods used are typically based on microwave digestion with mixtures of HCl, HF, $HClO_4$, $HNO_3$, $H_2O_2$... in pressurised bomb [9,12,13,16,19]. However, few papers indicate open system digestion for PGE determination in plant samples [10,17]. It appears interesting to make a comparison between the various approach (dry-ashing way and wet digestion way) used in the open digestion methods.

The aim of this study was to develop a complete method for the analysis of Pd, Pt and Rh in plant materials including the digestion procedure and the final determination by ICP-MS. USN was used as sample introduction system. Problems encountered in this instrumental configuration are rare. Therefore, although PGE content has been determined in different environmental compartments, their uptake by plants is still not fully investigated. The first objective is to investigate matrix effects resulting from concomitant elements present in plant samples for the determination of PGE.

The effects of major elements (K, Ca, Mg and P) encountered in plant digests on the analyte signals were studied at various concentrations. The aim of this simulation was to determine the most efficient internal standard to compensate the variations in analyte signal intensities [21]. Next, the correction was controlled using a plant material with increasing spikes of a PGE standard solution.

The aim of this investigation was also to compare five open digestion methods to prepare plant samples for determining their PGE concentrations. To our understanding, there is no study of this type available. Different digestion methods were compared to the determination of PGE in a recent study [25]. However, this study was carried out in a closed vessel with microwave technique and concerned only dust samples. Aqua regia digestion, $HNO_3$-$H_2O_2$ digestion, HF digestion following $HNO_3$-$H_2O_2$ digestion, dry-ashing and dry-ashing with HF attack were the proposed procedures tested on two plant samples. Digestions were carried out with and without additions of PGE in each sample to estimate the efficiency of the procedures and their reliability. PGE concentrations in solution and possible losses of analytes were measured and discussed for all methods.



## 2. Experimental

### 2.1 *Instrumentation*

The ICP-MS instrument used was a Thermo Electron X Series II (Thermo Elemental, Winsford, England) equipped with a CETAC (Omaha, Nebraska, USA) autosampler model ASX 500. The instrument used nickel sampling and nickel skimmer cones. The instrument was equipped with a standard one-piece torch with quartz injector tube (i.d.: 1.5 mm). An independent ultrasonic nebulizer U-5000AT+ (CETAC) equipped with a two-stage desolvation system was used. The liquid sample was pumped onto the face of the piezoelectric transducer driven by ultrasonic frequencies where it was converted to a fine and dense aerosol. The nebulizer gas flow transported the wet aerosol through a heated U-tube where the solvent was vaporised. Solvent vapours were then condensed by the thermo-electric cooler and removed by the drain pump to the waste. The sample output was sent directly to the spectrometer. Experimental conditions and mass calibration of the instrument were checked before analysis of samples with an autotune function. Details of experimental conditions are summarised in Table 1. Characteristics of the preferred isotopes analysed are summarised in Table 2 [26].

Table 1. Analytical parameters of ICP-MS.

| | |
|---|---|
| Power (kW) | 1.4 |
| Nebulization pressure ($L\,min^{-1}$) | 0.9 |
| Plasma gas flow ($L\,min^{-1}$) | 13 |
| Auxiliary gas flow ($L\,min^{-1}$) | 0.5 |
| Resolution (atomic mass unit) | 0.8 |
| Data acquisition | Triplicate |
| USN temperatures (°C) | 140/2 |
| Sample uptake rate ($mL\,min^{-1}$) | 1.2 |

### 2.2 *Reagents*

All reagents were analytical grade. All vessels were washed with 10% v/v $HNO_3$ and rinsed three times with purified water before use. Water purified (18 MΩ) with an ELGA (Bucks, UK) Purelab Ultra water purification system was used for all solutions. Commercial stock solution of Rh (1000 mg $L^{-1}$, standard solution for ICP) was obtained from Merck (Darmstadt, Germany). Commercial stock solutions of Pd and Pt (1000 mg $L^{-1}$, CRM Aqueous Calibration Solution) were obtained from Analytika (Prague, Czech Republic). For the digestion of plant samples, the reagents were $H_2O_2$ (30% Baker analysed), concentrated $HNO_3$ (69–70% Baker instra-analysed, for trace metal analysis), concentrated HCl (36.5–38% Baker instra-analysed, for trace metal analysis) and concentrated HF (48% Baker analysed).

The ICP-MS instrument was calibrated with a blank and four multi-element standard solutions prepared from stock solutions. The final concentrations in the standard solutions (acidified to 5% v/v with nitric acid) were, respectively, 20, 10, 5 and 2 μg $L^{-1}$. The linearity of the standards was satisfactory for all species ($r^2 \geq 0.99$) over this concentration range. An internal standard stock solution of 100 μg $L^{-1}$ of Bi, In, Ir and Y was prepared from single element stock solutions (standard solutions for ICP). For the determination by ICP-MS, all the samples were diluted two times to obtain solutions containing less than 5% (v/v) of acid. All solutions were spiked with the internal standard solution for a final concentration of 1 μg $L^{-1}$.



### 2.3 *Interference studies*

A stock solution containing the main matrix elements as than encountered in mineralised plant samples: K 1000 mg $L^{-1}$, Ca 500 mg $L^{-1}$, Mg 200 mg $L^{-1}$ and P 100 mg $L^{-1}$ and simulating plant matrix sample matrix was prepared in a 1000 ml volumetric flask. This stock solution was prepared from standard solutions (Merck Titrisol). Such concentrations are perhaps too high to represent real sample; in plant samples they may attain about half of these values at the most and the quarter on average. Parts of this synthetic matrix

Table 2. Spectroscopic data of measured isotopes.

| Isotopes | Abundance (%) | Ionisation potential (eV) | Main isobaric interferences |
|---|---|---|---|
| *Analytes* | | | |
| $^{103}Rh$ | 100 | 7.459 | $^{40}Ar^{63}Cu^+$; $^{87}Sr^{16}O^+$; $^{87}Rb^{16}O^+$ |
| $^{104}Pd$ | 11.1 | 8.337 | $^{40}Ar^{64}Zn^+$; $^{88}Sr^{16}O^+$; $^{104}Ru^+$ |
| $^{105}Pd$ | 22.3 | 8.337 | $^{40}Ar^{65}Cu^+$; $^{89}Y^{16}O^+$ |
| $^{108}Pd$ | 26.5 | 8.337 | $^{40}Ar^{68}Zn^+$; $^{92}Zr^{16}O^+$; $^{92}Mo^{16}O^+$; $^{108}Cd^+$ |
| $^{194}Pt$ | 33.0 | 8.959 | $^{178}Hf^{16}O^+$ |
| $^{195}Pt$ | 33.8 | 8.959 | $^{179}Hf^{16}O^+$ |
| $^{196}Pt$ | 25.2 | 8.959 | $^{180}Hf^{16}O^+$ |
| *Internal standard* | | | |
| $^{89}Y$ | 100 | 6.217 | |
| $^{115}In$ | 95.7 | 5.786 | |
| $^{193}Ir$ | 62.7 | 8.967 | |
| $^{209}Bi$ | 100 | 7.286 | |

solution were added into 100 mL volumetric flasks in the following proportions: 0 mL (pure trace multi-element solution), 10 mL, 20 mL, 40 mL and 80 mL. Each solution was acidified to 5% v/v with concentrated nitric acid. 2 mL of a standard solution containing 100 $\mu g\,L^{-1}$ of the researched elements were added to each flask before completion with purified water to a constant volume.

Each solution was quantified in triplicate with external standardisation. Relative intensities were expressed as the ratios of the concentration obtained in the matrix solutions to this obtained in the pure solution. To overcome the analytical bias due to possible contamination from matrices, the matrix solutions were also prepared without addition of PGE solution and analysed as blanks. The values obtained for all elements studied were subtracted from the values obtained for the spiked solutions. This procedure allows determining the effects of progressively increasing amounts of plant matrix on the analytical response of trace elements studied and their correction by internal standardisation. For indication, the levels of the blanks measured were, respectively, $0 \leq Rh \leq 0.002\,\mu g\,L^{-1}$; $0.012 \leq Pd \leq 0.063\,\mu g\,L^{-1}$; $0 \leq Pt \leq 0.003\,\mu g\,L^{-1}$ according to the amount of salts in solutions.



### 2.4 *Recoveries study in plant sample analysis*

The accuracy of the determination method was controlled using a usually cultivated plant sample (maize, entire plant). The sample was digested many times with blanks. Two additions of a standard solution containing 100 $\mu g\ L^{-1}$ of the researched elements were added, after the digestion, in certain solutions (respectively 0.5 and 10 mL to obtain final added concentrations of 0.5 and 10 $\mu g\ L^{-1}$). In final, we have three different plant digestion solutions with three replicates each, one without addition and two with addition in volumetric flasks. The aim of this investigation was to verify that the final determination of PGE was relevant on a true sample. Here, the recoveries study was an estimation of the systematic error of the ICP-MS method.

For digestion, dry plant sample (1.0 g) was weighed in to a 250 mL Pyrex glass tube. Then 5 mL of nitric acid and 10 mL of hydrogen peroxide were added. After 16 hours (overnight) of cold digestion, the tubes were equipped with a cooling system and heated with reflux during a period of 2.5 h. The heating block was raised to 270°C. The acid mixture was thereafter filtered through ash-free paper filter (Whatman filter paper 40) into a 100 mL volumetric flask and made up with purified water.

### 2.5 *Recoveries study for digestion procedures*

The efficiencies of various digestion methods were tested on two types of plant materials (maize and oak leaves). These two samples are usually used as control samples in our lab and are available in large amount. Digestions were carried out with and without addition of PGE. Two additions of the standard solution containing 100 $\mu g\,L^{-1}$ of the researched elements were added in certain samples before digestion (respectively 0.5 and 10 mL to obtain final added concentrations of 0.5 and 10 $\mu g\,L^{-1}$). The aim of this investigation was to determine the recovery the whole analytical procedure. Each sample was digested with three replicates for each one and blanks. The five digestion methods are described in Table 3. In all procedures, approximately 1.0 g ($1.0 \pm 0.1$ g) of dried plant material was weighed.

Method I ($HNO_3$–$H_2O_2$) is described in the above section. The same procedure was used for the aqua regia digestion (Method II) but with 2.5 mL $HNO_3$ and 7.5 mL HCl. The dry-ashing method (Method III) was obtained by incinerating dry plant sample in a silicon capsule at 480°C for five hours in a muffle furnace and solubilising the sought elements, present in ash, with 5 mL $HNO_3$ on a hot plate. The solution was filtered into a 100 mL volumetric flask and adjusted with purified water. Method IV started as the dry-ashing method. After incineration, the sample was transferred in a Teflon capsule and 5 mL HF were added. After evaporation on a hot plate, the residue was taken up with 5 mL $HNO_3$, filtered into a 100 mL volumetric flask and adjusted with purified water. Method V followed, at first, the same procedure as Method I. After the filtration of the acid mixture into a 100 mL volumetric flask, the ash-free paper filter was incinerated at 550°C for two hours in a silicon capsule. The residue was treated by HF as in method IV. The filtered solution was added to the first digested solution and adjusted to 100 mL with purified water. For indication, the levels of the blanks measured are indicated in Table 3.

## 3. Results and discussion

### 3.1 *Interference studies*

The relative intensities of $^{103}Rh$, $^{105}Pd$ and $^{196}Pt$ were calculated without IS as the means and standard deviations on the three replicates. Results are presented in Figure 1 (diagrams a, b and c, no IS) depending on the addition rate of the matrix solution. The other isotopes of Pd and Pt presented the same profile (data not shown). The isobaric interferences were found negligible. Accurate analyses require that any change in the matrix composition does not result in a significant variation in the analytical signal (max. 10%). However, accuracy was degraded when matrix mismatch occurs between the standard and the unknown solutions. Without exception, suppression of the analytical signals was a function of increased concomitant concentration. The results were in



Table 3. Description of the digestion methods I, II, III, IV and V and background levels of the digestion blanks (mean of triplicate, in ng $L^{-1}$).

| | Method I | Method II | Method III | Method IV | Method V |
|---|---|---|---|---|---|
| Stage 1 | 5 mL $HNO_3$<br>10 mL $H_2O_2$ | 2.5 mL $HNO_3$<br>7.5 mL HCl | Dry ashing<br>480°C | Dry ashing<br>480°C | 5 mL $HNO_3$<br>10 mL $H_2O_2$ |
| Stage 2 | Filtration | Filtration | 5 mL $HNO_3$ | 5 mL HF | Filtration |
| Stage 3 | | | Filtration | 5 mL $HNO_3$ | Dry ashing of filter |
| Stage 4 | | | | Filtration | 5 mL HF<br>5 mL $HNO_3$ |
| Stage 5 | | | | | Filtration |
| Levels of blanks ($n = 3$) | | | | | |
| $^{103}Rh$ | ≤1 | ≤1 | ≤1 | ≤1 | ≤1 |
| $^{105}Pd$ | 17 | 8 | 4 | 12 | 21 |
| $^{196}Pt$ | 2.6 | ≤1 | ≤1 | ≤1 | 5 |

agreement with previous observations in ICP-MS [21,22]. In the most unfavourable case (for Pt), the degradation attained about 60% depression in the presence of the heaviest matrix.

Several factors contributed to the reduction of analytical signals. Changes in the plasma properties in the presence of high salt matrix type [27], effects of easily ionisable elements such as K, Ca and Mg, rich in plant samples [21,28], or space-charge effects [28] could explain these suppressions.



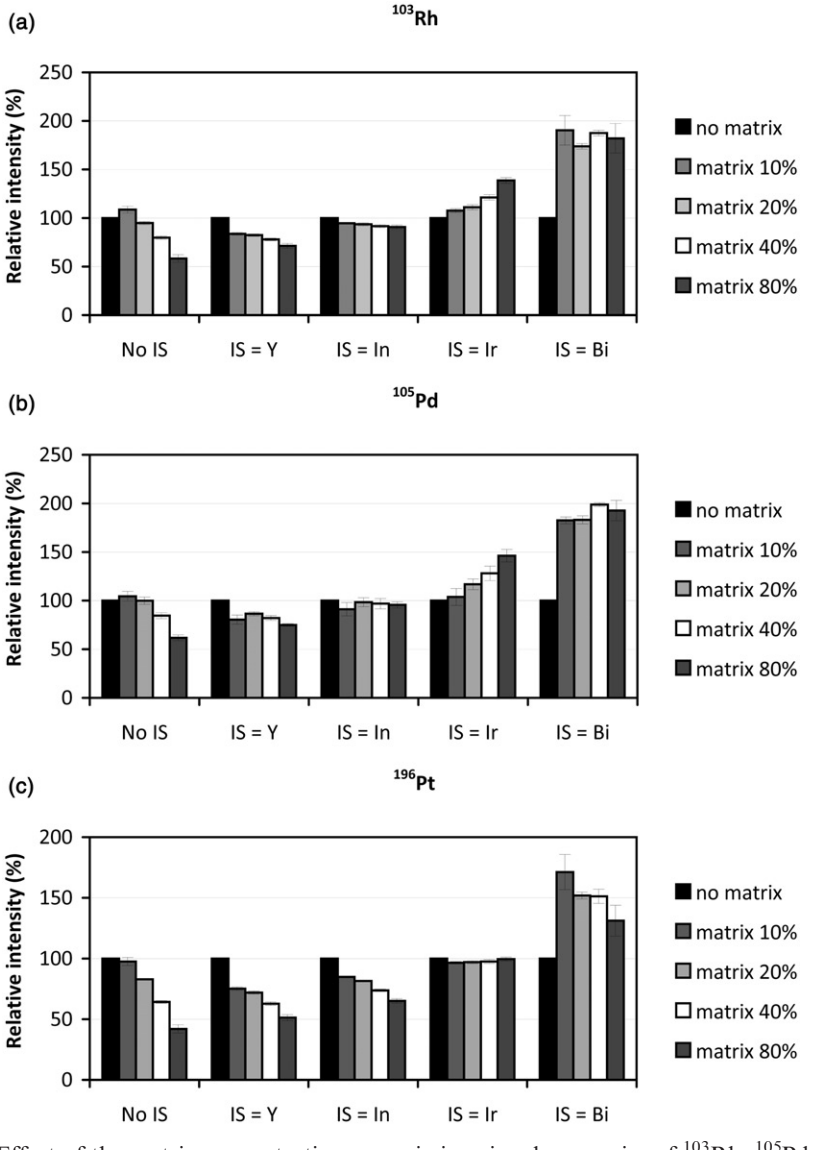


Figure 1. Effect of the matrix concentration on emission signal recoveries of $^{103}$Rh, $^{105}$Pd and $^{196}$Pt with and without various internal standards. The basis of the relative intensity was: no matrix = 100% recovery. Means and standard deviations ($n = 3$) are presented.

### 3.2 *Internal standardisation/recoveries study*

A consequence of the variable response of analytical elements to matrix amount was the need to apply several internal standards (IS) to compensate these interferences. The recoveries of Pd, Pt and Rh were studied in function of various internal standards (Bi, In, Ir and Y). Details of internal standard elements applied to the experiment are given in Table 2.

In appeared as the best IS for Rh in practice and the corrections were satisfactory (Figure 1a). Using Y as IS, the error on the recoveries remained severe for Rh. For IS with higher mass such as Ir or Bi, data show overestimated concentration measurements for the concentrated matrix solutions. The behaviour of Pd was typically the same as Rh (Figure 1b). The two elements are close both for mass number and ionisation energy. High recoveries of Pd concentrations were then obtained with In as IS on the simulation solutions. Y, Ir and Bi provided unacceptable recoveries. For Pd determination, it was expected that the $^{105}$Pd isotope suffered from the interference of $^{89}Y^{16}O^{+}$. However, this trend was not necessary consistent with the observed results because the oxide rate in the plasma was strongly reduced with the use of USN. The typical results obtained for Pt with internal standards are presented in Figure 1(c). Using Y or In, the matrix effect was reduced but not entirely corrected. Conversely, high recoveries of Pt concentration were obtained, close to 100%, for all synthetic solutions tested when Ir was used as IS. Using Bi as IS, the signal of Pt ions was significantly improved by concomitant concentrations. It must be noted that Ir is also deposited along roads with Pt, Pd and Rh as impurity in car catalysts and is also being used in some diesel car catalyst [14,15]. However, Ir remains in very low concentrations in plant samples (less than $0.4\,ng\,g^{-1}$) [14] and does not influence the concentration of internal standard.

The effectiveness of In and Ir as IS was verified by the analysis of the three elements studied in a maize plant sample spiked with two additions of standard solution. Results are presented in Table 4. In all cases, the analytical results obtained for the reference plant sample were comparable to the corresponding spikes. The error was generally less than 10%. The concentrations measured for Pd appeared slightly overestimated but remained satisfactory. This was in accordance with the interference studies. The simulation results might help to remove the matrix effects for digested plant samples. However, accurate determination of PGE in plant requires an efficient digestion method for plant materials.



Table 4. Recovery in $\mu g\,L^{-1}$ of additions in maize sample solutions after wet digestion with $HNO_3$–$H_2O_2$ (IS = In for Rh and Pd, Ir for Pt).

| Isotope | $^{103}$Rh | $^{104}$Pd | $^{105}$Pd | $^{108}$Pd | $^{194}$Pt | $^{195}$Pt | $^{196}$Pt |
|---|---|---|---|---|---|---|---|
| Addition $0.5\,\mu g\,L^{-1}$ | | | | | | | |
| Mean ($n=3$) | 0.48 | 0.58 | 0.59 | 0.62 | 0.47 | 0.47 | 0.47 |
| s ($n=3$) | 0.02 | 0.04 | 0.04 | 0.06 | 0.02 | 0.02 | 0.02 |
| Addition $10\,\mu g\,L^{-1}$ | | | | | | | |
| Mean ($n=3$) | 9.06 | 10.76 | 10.78 | 10.85 | 9.07 | 9.08 | 9.13 |
| s ($n=3$) | 0.51 | 0.24 | 0.23 | 0.21 | 0.32 | 0.35 | 0.32 |

### 3.3 *Digestion methods*

The main problem in the determination of PGE is the lack of certified reference materials for quality control. The reference materials available are different types of minerals, recycled monolith autocatalyst and road dust where the concentrations of PGEs are generally higher than in plant materials (autocatalyst) and the matrix composition are very different [14,29]. In these conditions, the recoveries of Pd, Pt and Rh were studied by adding known amounts of elements (0.05 and 1 μg) to maize samples before digestion. The samples were digested with various methods and recoveries for analytes were calculated after ICP-MS measurements.

Table 5 shows the experimental results obtained on the maize sample for $^{103}$Rh, $^{105}$Pd and $^{196}$Pt, respectively. Several differences were observed between the digestion methods. The use of $HNO_3$ or HF to make soluble PGE after dry-ashing appeared not relevant and Methods III and IV suffered from severe losses of PGE (especially Pd). These results can be interpreted by the formation of insoluble compounds e.g. PdO which are insoluble in the concentrated acids used [26]. Generally, the hydrofluoric treatment allows dissolving elements, which may be retained by the insoluble silica residue of the sample [23]. However, when the above digestion method was continued with HF attack, recoveries of PGE were not significantly improved (Method IV).

The recoveries obtained for the wet digestion method with $HNO_3$–$H_2O_2$ (Method I) were largely better than those obtained after dry-ashing of plant samples. The recoveries obtained for Pt and Rh were generally very good. Inversely, only a 69% recovery was obtained on the $10\,\mu g\,L^{-1}$ addition for Pd. The loss may be explained by the possible formation of PdO during the digestion. However, it can be expected that PGE concentrations in plants are at a much lower concentration level than $10\,\mu g\,L^{-1}$. When this wet digestion method was continued with HF (Method V), similar results were observed for Rh and Pt and more important losses occurred for Pd. The formation of oxides may be carried out by reaction of palladium fluoride ($PdF_2$) with $H_2O$ and could explain the differences [26].

The aqua regia digestion by $HNO_3$–HCl (Method II) gave acceptable results for Rh, Pd and Pt. The results of the spiked samples indicated that there were no important losses of Pd, Pd and Rh during the digestion. The mixture $HNO_3$–HCl is a very oxidizer



Table 5. Comparison of PGEs recoveries (in %) in maize sample solutions for all digestion procedures. The additions were made before digestion (IS = In for Rh and Pd, Ir for Pt).

| Addition ($\mu g\,L^{-1}$) | Method I | Method II | Method III | Method IV | Method V |
|---|---|---|---|---|---|
| $^{103}$Rh | | | | | |
| 0.5 | 97 (1) | 93 (2) | 48 (8) | 57 (3) | 89 (3) |
| 10 | 95 (2) | 93 (11) | 58 (2) | 68 (2) | 106 (14) |
| $^{105}$Pd | | | | | |
| 0.5 | 109 (9) | 87 (3) | 4 (2) | 20 (16) | 105 (7) |
| 10 | 68 (4) | 90 (9) | 3 (1) | 17 (2) | 49 (9) |
| $^{196}$Pt | | | | | |
| 0.5 | 94 (1) | 92 (3) | 28 (2) | 46 (4) | 92 (4) |
| 10 | 98 (2) | 105 (12) | 25 (2) | 30 (2) | 109 (12) |

Note: The value in the bracket represents the standard deviation ($n = 3$).

Table 6. Comparison of PGEs recoveries (in %) in oak leaves sample solutions for the wet digestion procedures. The additions were made before digestion.

| Addition ($\mu g\,L^{-1}$) | Method I | Method II | Method V |
|---|---|---|---|
| $^{103}Rh$ | | | |
| 0.5 | 90 (2) | 93 (6) | 75 (2) |
| 10 | 96 (4) | 110 (15) | 79 (3) |
| $^{105}Pd$ | | | |
| 0.5 | 117 (3) | 87 (8) | 100 (5) |
| 10 | 74 (7) | 104 (14) | 63 (3) |
| $^{196}Pt$ | | | |
| 0.5 | 95 (3) | 91 (5) | 87 (3) |
| 10 | 100 (5) | 105 (13) | 84 (3) |

Note: The value in the bracket represents the standard deviation ($n = 3$).



environment and can drive to the solubilisation of many elements in many materials such as gold metal. Many papers report that dissolution in aqua regia was the most suitable method for complex matrices [30]. For all digestion methods, similar results were obtained with the other Pd and Pt isotopes (data not shown). The isobaric interferences were then found negligible with this plant sample.

The effectiveness of wet digestion was verified by the analysis of the three elements studied in an oak leaves sample with the two additions of standard solution. Presented in Table 6, results were satisfactory for aqua regia. Therefore, the relative standard deviations (generally lower than 15%) indicated the feasibility of using this method. The initial additions were also found again for Rh and Pt with wet digestion. However, as for the maize sample, losses occurred for Pd on the $10\,\mu g\,L^{-1}$ addition samples. It can be expected that this last concentration is perhaps too high to represent real sample. In these conditions, the wet digestion is suitable.

### 3.4 *Plant samples*

One part of the study was to determine the PGE concentrations in plant samples. Various plant samples were collected along the A62 highway in the area of Cestas, France. Previous investigations indicate that plants along highways accumulate PGE [11,12], Mushrooms, dandelions, mosses and ferns were collected as test samples. It should be noted that mushrooms are not exactly plants (they cannot photosynthesis) but they are suitable bio-indicators. Dust and soil particles were cleaned from the samples with de-ionised water, dried at 103°C to constant weight, ground to a homogeneous fine powder and subjected to digestion and analysis.

The aim of this limited sampling was to obtain preliminary information about the anthropogenic PGE emissions. The aim of this investigation was also to select the most interesting plant material for use as bio-indicators for further investigations in following years. The selected samples, mushrooms, dandelions, mosses and ferns were digested with aqua regia. The results are shown in Table 7. The uncertainties obtained on the measured concentrations were extremely large. Few statistically significant differences were found between the samples. The high uncertainties were due to the random sampling of samples

Table 7. Concentrations in ng $g^{-1}$ of PGEs measured in various plant materials.

| Isotope | $^{103}Rh$ | $^{105}Pd$ | $^{196}Pt$ |
|---|---|---|---|
| Mushrooms | $0.6 \pm 0.3$ | $7.9 \pm 1.8$ | $17.6 \pm 14.4$ |
| Fern | $0.3 \pm 0.1$ | $5.7 \pm 2.3$ | $2.3 \pm 0.4$ |
| Mosses | $1.2 \pm 0.2$ | $27.6 \pm 7.6$ | $14.1 \pm 8.8$ |
| Dandelions | $0.6 \pm 0.4$ | $12.3 \pm 10.6$ | $4.3 \pm 3.1$ |

Table 8. Detection limits (ng $L^{-1}$).

| | |
|---|---|
| $^{103}Rh$ | 0.4 |
| $^{105}Pd$ | 1.0 |
| $^{196}Pt$ | 2.0 |



and were not due to the analytical method. Pd appeared as the most bioavailable element for plants [5]. Pt appeared as the most present element in mushrooms. In comparison with Pd and Pt, Rh appeared as the least present element in plant materials. However, the measured concentrations of Rh showed that this element is accumulated to a greater extent in mosses than in other plant materials. For this last reason, mosses appeared perhaps as the best choice of samples to monitor the bioaccumulation of PGE over time. Mosses are present in most terrestrial habitats and are often cited in literature as the samples which best reflected the level of pollution [9,12]. However, the results were obtained from a single sampling point and no comparison with other places was achieved. The level of pollution was then difficult to establish. Therefore, the concentrations of PGE present in plant depend both on the PGE bioavailability and on the PGE concentrations emitted by cars.

Table 8 shows the detection limits obtained for the ICP-MS method. Limit of detection is defined as the lowest concentration of analyte that can be reliably distinguished from blank. The detection limits were calculated as three times the standard deviations of the blanks which were determined by measuring 20 times a sample of distilled water in 5% v/v $HNO_3$. It was clear that the performances showed high sensitivity.

## 4. Conclusions

The investigations developed an accurate method suitable for the analysis of Pd, Pt and Rh in plant samples. The results demonstrated the applicability of ICP-MS spectrometry coupled with USN for the determination of elements provided that the matrix interferences are corrected. In fact, it was established experimentally that matrix effect resulting from moderate amounts (0.2–2%) of a mixture components changed analyte signals significantly. Accurate measurements must be restored by using internal standards which corrected the matrix suppression. However, the appropriate selection of IS was the primary cause of accuracy of analysis and careful attention must be provided for this choice. The investigations show also that it is possible, by using wet digestion, especially with aqua regia or $HNO_3$–$H_2O_2$, to put all the Pd, Pt and Rh in solution. Using dry-ashing procedure followed by $HNO_3$ or HF treatment of ashes, losses of PGE were generated,

providing erroneous measurements. Due to improved detection power with USN, analysis of plant material may be routinely considered. However, the concentration of concomitants encountered in plant samples was relatively low and does not correspond to the maximum matrix influence that could be obtained for other environmental samples such as soils or wastes.

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