Determination of Rh, Pd and Pt in urine samples using a pre-concentration sequential injection analysis system coupled to a quadrupole-inductively coupled plasma-mass spectrometer

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A B S T R A C T

The proposed flow system was developed in order to minimize the drawbacks related to the PGEs determination by quadrupole-inductively coupled plasma-mass spectrometry (Q-ICP-MS). It was intended not only to lower the limits of detection (LODs) but also to eliminate the interferences originating from some atomic and molecular ions produced in the argon plasma. This was accomplished by means of an on-line sample clean-up/pre-concentration step, using a chelating resin (Metalfix™ Chelamine™) in which Rh, Pd and Pt were preferably retained when compared with the interfering species.

The results obtained by using the developed flow system in the analysis of urine samples are presented. With a sampling rate of 9 samples h⁻¹ (i.e., 27 determinations) and a sample consumption of ca. 10 mL, the developed flow system allowed linear calibration plots up to 100 ng L⁻¹ with detection limits of 1.2 ng L⁻¹ (Rh), 0.4 ng L⁻¹ (Pd) and 0.9 ng L⁻¹ (Pt). Repeatability studies showed good precision (R.S.D., n = 5): 3.7% (Rh); 2.6% (Pd) and 2.4% (Pt), for 10 ng L⁻¹; 2.4% (Rh); 1.4% (Pd) and 1.9% (Pt), for 50 ng L⁻¹; and 1.3% (Rh); 0.58% (Pd) and 0.62% (Pt), for 100 ng L⁻¹. By spiking human urine samples, recovery tests were performed, and the values obtained ranged between 89% and 105% (Rh); 90% and 104% (Pd); and 93% and 105% (Pt).

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1. Introduction

Because of their chemical inertness, platinum group elements (PGEs), which belong to the noble metals group, have been considered harmless for a long time [1]. However, over the past few years, PGEs have become widely used and, for that reason, their release into the environment has increased considerably. PGEs are being used: (i) in catalytic converters (Pt, Pd and Rh) of car exhaust systems to remove carbon monoxide, unburned hydrocarbons and nitrogen oxides; (ii) in dental restorative alloys; and (iii) as catalysts in numerous chemical syntheses. These actions led to an increased release of PGEs into the environment and to the appearance of these metals as residues in many products used daily, such as foods and pharmaceuticals [1]. The concerns over the potential biological effects of this environmental accumulation of
PGEs instigate the scientific community attention for their determination in biological samples, in order to evaluate possible risks for human health [1-4].

Due to the very low concentration (parts per trillion range) of PGEs in biological samples, which are complex matrices, and to their chemical behaviour, related with the fact of belonging to the noble metals group, the PGEs levels in biological samples are difficult to evaluate [4,5]. Although there are several techniques that can be used for PGEs determination [5-7], their background levels are mostly studied using graphite furnace atomic absorption spectrometry (GFAAS) [1,8], and, more recently, inductively coupled plasma-atomic emission spectrometry (ICP-AES) [9,10], and, specially, inductively coupled plasma-mass spectrometry (ICP-MS) [3,11-17], as can be perceived by the increasing number of scientific publications. When compared with GFAAS, ICP-MS has clearly noticeable advantages due to the fact of being a rapid and sensitive technique that also allows multi-element analysis. These characteristics make ICP-MS particularly well suited for the determination of PGEs. However, the formation of spectral interferences originating from atomic and molecular ions produced in the argon plasma (e.g., $^{40}$Ar$^{65}$Cu on $^{105}$Pd; $^{106}$Cd and $^{40}$Ar$^{66}$Zn on $^{106}$Pd; $^{108}$Cd on $^{108}$Pd; $^{87}$Sr$^{16}$O, $^{40}$Ar$^{63}$Cu and $^{206}$Pb$^{2+}$ on $^{103}$Rh) plagues the quantification of some of these ultra-trace elements, especially when low-resolution quadrupole ICP-MS (Q-ICP-MS) is used and, above all, when complex matrices (e.g., high saline matrices) are to be analysed [10,17,18].

The aim of this work was both to eliminate the interferences in PGEs determination by Q-ICP-MS and to lower the limits of detection (LOD). This was accomplished by performing an on-line sample clean-up/pre-concentration step in a sequential injection analysis (SIA) system incorporating a column filled with a chelating resin – Metalfix$^\text{TM}$ Chelamine$^\text{TM}$ – in which PGEs were preferentially retained when compared with the interfering species [10,19-21].

## 2. Experimental

### 2.1. Reagents and solutions

In the preparation of all solutions, high quality water (resistivity higher than 18 MΩ cm$^{-1}$) obtained through a Milli-Q$^\text{TM}$ system (Millipore; Billerica, Massachusetts, USA) was used. All the reagents used were of analytical grade, except for nitric and hydrochloric acids, which were of Suprapur$^\text{®}$ grade (Merck).

Rh, Pd and Pt standard solutions were prepared by appropriate dilution of the respective single element 1000 mg L$^{-1}$ standard stock solutions (Fluka; Buchs, Switzerland) with a 0.2 M aqua regia solution. To evaluate the influence of co-existing metals, single element 1000 mg L$^{-1}$ standard stock solutions (BDH; Poole, England) were used.

The pre-concentration column was filled with Metalfix$^\text{TM}$ Chelamine$^\text{TM}$ resin (particles diameter: 40–80 μm), supplied by Fluka, which is obtained by immobilization of a pentamine ligand (tetraethylene pentamine) in an organic polymer (reticulate polyacrilamide) [22].

### 2.2. Instrumentation

PGEs determination was performed by using a VG Elemental (Winsford, UK), PlasmaQuad 3 ICP-MS, equipped with a Meinhard$^\text{®}$ type A pneumatic concentric nebulizer, a quartz water cooled impact-bead spray chamber, a standard quartz tube torch and nickel sample and skimmer cones. Both the spray chamber and sampling interface were cooled to 10°C by circulating water. Argon of 99.9999% purity (Alphagaz 2$^\text{TM}$, supplied by Air Liquide, Maia, Portugal) was used as plasma source. For ICP-MS waste draining, a Gilson (Villiers-Le Bel, France) peristaltic pump was used. The main operating conditions for ICP-MS determinations are indicated in Table 1. The instrument was daily tuned for maximum signal sensitivity and stability using $^{115}$In as the target isotope. The elemental isotopes (m/z ratios) $^{103}$Rh, $^{105}$Pd and $^{195}$Pt (as analytical isotopes) and $^{115}$In (as internal standard) were monitored. The ICP-MS operation and data acquisition was accomplished by using PlasmaLab software.

A microwave oven, MLS-1200 Mega (Milestone; Sorisole, Italy), equipped with a HPR-1000/10 S rotor was used for urine samples digestion.

### 2.3. Flow system description and operation

The SIA system (Fig. 1) comprised a Crison (Barcelona, Spain) module (consisting of an 8-port selection valve), two Gilson peristaltic pumps equipped with PVC propulsion tubing with 0.76 mm i.d. (PP1) and 2.06 mm i.d. (PP2), two three-way solenoid valves (NResearch Inc., West Caldwell, NJ, USA), Omninfit (Cambridge, United Kingdom) PTFE tubing (0.8 mm i.d.), a heating plate, a home-made Perspex pre-concentration column (small tube with 3 cm length, 3 mm i.d.) [24] and connectors. The extremities of the pre-concentration column were sealed with Teflon$^\text{®}$ filters (MoBiTec; Goettingen, Germany) with 35 μm pore size. Both column ends were threaded, thus enabling the connection to the flow system by means of Gilson conventional threaded connectors [24].

The control of the analytical system as well as data acquisition and processing was performed by means of a personal computer equipped with a Pentium-III processor and...
a PCL-711B PC-MultiLab Interface Card (Advantech Co. Ltd.; Taipei, Taiwan). Software was developed in QuickBasic® 4.5.

The different steps of the analytical cycle used in Rh, Pd and Pt determination are summarized in Table 2. The first step was the sample channel cleaning (step 1). This step comprised (i) the propelling of the water that remained inside the flow system after the 5th step of the preceding analytical cycle, followed by the propelling of air, both from waste channel to SIA valve port 3 (step 1.t), and (ii) the aspiration of water from SIA valve port 8 to waste (step 1.2). The following step (step 2) – the pre-concentration step – involved the sample loading into the pre-concentration column, where Rh, Pd and Pt were retained. After that, air was aspirated, also towards waste, in order to eliminate, before elution, the volume of sample that was still inside the flow system (step 3). Then, Rh, Pd and Pt retained into the pre-concentration column were eluted in a reverse mode (step 3). Finally, water was aspirated, from SIA valve port 8, through the column towards waste (step 5).

The peristaltic pump PP1 was continuously aspirating water to “feed” the ICP-MS nebuliser uptake rate throughout the whole analytical cycle, excepting for the step 3 during which it was stopped. The peristaltic pump PP2 was the only device that was responsible by the flow management of the pre-concentration system itself.

<table>
<thead>
<tr>
<th>Table 2 – Flow system operation</th>
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<tr>
<td>Step</td>
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<tr>
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<td>4</td>
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<td>5</td>
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</tbody>
</table>

Legend: SIAv, 8-port selection valve; PP1 and PP2, peristaltic pumps; SV1 and SV2, three-way solenoid valves; a, aspirating; p, propelling; s, stopped; c, closed; o, opened.

3. Results and discussion

3.1. Development and optimisation of the flow system

3.1.1. Pre-concentration from different acidic media

Pohl et al. [10] have already evaluated the sorption of noble metals (Au, Ir, Pd, Rh and Ru) by Metalfix™ Chelamine™ from different acidic media. They performed a wide evaluation (different acids, isolated or as a mixture; different H⁺ concentration) with the resin as particles of 150–300 μm size, but for Metalfix™ Chelamine™ of 40–80 μm particle size they only had tested the noble metals sorption when preparing PGEs solutions with HCl solution of different H⁺ concentration. For such particle size (40–80 μm), they described retention efficiencies closer to 100% for Pd and Pt, and ca. 50% for Rh, when using solutions prepared with HCl ranging from 0.2 M to 1.0 M.

In this work, to evaluate the retention efficiency of the PGEs by the Metalfix™ Chelamine™ of 40–80 μm particle size, standard solutions of 0.5 μg L⁻¹ and 1 μg L⁻¹ were prepared in different acidic media and tested. These standard solutions were prepared in HCl (0.2, 0.5, 1.0, 1.5, 2.0 and 3.0 M); HNO₃ (0.2, 0.5, 1.0, 1.5, 2.0 and 3.0 M); or a mixture (1:1) of HCl and HNO₃ (with a total H⁺ concentration of 0.2, 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 M); or a mixture (3:1) of HCl and HNO₃ (with a total H⁺ concentration of 0.2, 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 M). The evaluation of the retention efficiency was performed in on-line mode, i.e., the signal was monitored in the derived effluent during the pre-concentration step and compared with the signal obtained by direct introduction of the same standard solutions.

The retention efficiency for Rh was lower than 50% for all the studied solutions. Although it slightly increased with the increasing acid concentration, the precision of the results was better when using HCl and HNO₃ (3:1) solution with a H⁺ concentration between 0.2 M and 1.0 M. Conversely, Pt retention efficiency lowered considerably with the increasing in the acid concentration, and also when the composition of the acidic media changed (retention efficiency ranged between 20% and 100%). Retention efficiency closer to 100% was only attained when a mixture of HCl with HNO₃ (3:1) with an H⁺ concentration between 0.2 M and 1.0 M. Finally, the results obtained for Pd were similar to those obtained by Pohl et al. [10] when working with Metalfix™ Chelamine™ of 150–300 μm particle size, i.e., Pd almost was not affected either by the composition of the acidic media or by the H⁺ concentration.
concentration (retention efficiency varying between ca. 95% and 100%).

The best compromise between precision and retention efficiency for the three metals under study was standards and samples acidification with the HCl and HNO₃ (3:1) mixture. The H⁺ concentration could vary between 0.2 M and 1.0 M without significantly affecting Rh, Pd and Pt retention by Metalfix™ Chelamine™ of 40–80 μm particle size.

3.1.2. Column
Columns with different lengths (3–7 cm) and internal diameters (2–4 mm) were tested. It was verified that the sensitivity decreased when increasing columns length. In fact, for the same pumping conditions, increasing columns length impaired the sample volume that was introduced into the flow system due to a more pronounced backpressure effect. On the other hand, by increasing columns internal diameter, it was verified that reproducibility decreased. Thus, and as a compromise between sensitivity and precision a column with 3 cm length and 3 mm of internal diameter was selected.

3.1.3. Pre-concentration flow rate
The pre-concentration flow rate was optimized through the monitoring of the column effluent. This was accomplished by analysing the waste produced during the pre-concentration step (passage of the sample through the column) of a 1 μL⁻¹ standard solution during 120 s. Each new cycle, during the pre-concentration step, this solution was aspirated by the peristaltic pump PP₂ at different flow rates (1–7 mL min⁻¹) through the column. The respective wastes were collected separately, and then were analysed by ICP-MS. Since they gave similar results, it was concluded that the flow rate did not influence the retention efficiency. Nevertheless, when using flow rates higher than 4 mL min⁻¹ the irreproducibility of the volumes pumped by the peristaltic pump increased considerably. Therefore, a flow rate of 4 mL min⁻¹ was selected.

3.1.4. Sample volume
Once established the pre-concentration column’s length and internal diameter, and the pre-concentration flow rate, it was important to set up the volume of sample that was allowed to pass along the column towards waste without saturating the mass of resin packed into the column. By aspirating, at 1 mL min⁻¹ flow rate, during 30 min, an Rh, Pd and Pt 10 μg L⁻¹ standard solution through the column, and continuously monitoring the column effluent, it was possible to conclude that the mass of resin inside the column had not become saturated, since the column effluent did not suffer any variation in its composition along time. Being so, the mass of resin packed into the column would not constitute a limiting factor when selecting the volume of sample to be pre-concentrated. Thus, different sample volumes (5–20 mL) were tested and its selection was made taking into consideration both sensitivity and sampling rate. Since sample volume is defined both by the sampling time and the peristaltic pump flow rate (already set at 4 mL min⁻¹), a sampling time of 150 s, corresponding to a sample volume of ca. 10 mL, was selected. The selected volume allowed adequate sensitivity for PGEs determination without considerably impairing the sampling rate.

3.1.5. Buffer solution/sample pre-treatment
The PGEs retention behaviour on Metalfix™ Chelamine™ is pH dependent [19–21]. Since urine samples could present significantly different physiological pH values, it was important to “equalize” the pH of the samples. For that purpose, the on-line addition of a HCl/KCl buffer solution was tested. According to Igesias et al. [19] in relation with the optimum pH for PGEs retention by Metalfix™ Chelamine™, the pH values that were tested ranged from 1.0 to 2.5. Nevertheless, it was concluded that the on-line buffering step was avoidable. In fact, in order to obtain the analytes dissolved in acidic solutions, urine samples were digested; and studies involving sample pre-treatment revealed that the microwave oven digestion of 12 mL of urine with 3 mL of aqua regia at 500 W during 5 min and the addition of 10 mL of aqua regia 0.2 M H⁺ after the digests cooling to room temperature resulted in solutions with similar acidic pH values. Further, when comparing the results obtained in the analysis of the samples obtained after microwave oven digestion (“direct” analysis, i.e., “digested samples” analysed with no further treatment), and in the analysis of those same samples but subjected to a posterior on-line “buffering treatment”, it was possible to conclude that in the former case the results presented lower R.S.D.% values (ca. 50%). In addition, the “direct” analysis of the samples after its microwave oven digestion resulted in a SIA flow manifold with a simpler configuration and allowed higher sampling rates.

3.1.6. Pre-elution washing step
A washing step before the elution step was tested. The main objective was to eliminate the sample that still remained inside the flow system after the pre-concentration step. Initially, this washing step was carried out with the blank solution; then, Milli-Q water was also tested. It was verified that the use of a liquid to “wash” the sample from inside the flow system to waste impaired peak shape (larger peaks, sometimes presenting a “serrated” profile and/or presence of double-peaks) and, thus, the flow system’s performance (sampling rate, precision and accuracy). Despite the fact that the presence of air can theoretically generate plasma instability, in practice, this was not significant. In fact, when using air to push the sample to waste, the peaks were narrower, the time needed for the elution step diminished (improving sampling rate), double-peaks never occurred and the flow system’s precision and accuracy were both enhanced.

The behaviour of the flow system when changing from a washing step with a liquid to a washing step with air could probably be related with the fact that by using air there was no effect of dispersion/dilution of the eluate, hence improving detection; furthermore, the air that reached the plasma propelled by the eluent did not create any instability most likely because of the air plug small dimensions (the nebuliser uptake rate was being continuously “fed” by peristaltic pump PP₂ until the elution step and, as the air plug that was introduced before the sample was small, it was not sufficient to generate a significant plasma disturbance).

3.1.7. Elution step
3.1.7.1. Eluent composition. Metalfix™ Chelamine™ is a pentamine resin that provides a high rate of adsorption for noble
metals making it possible to separate them from other metals [19–21]. Although the high affinity showed by this resin for PGEs is considered to be useful during the pre-concentration step, it becomes a drawback during the elution step, as it makes difficult the release of PGEs from the resin [25]. Thus, different eluents were tested in order to find the best alternative in terms of recovery, precision and flow system operation/sampling rate.

Considering the results of Iglesias et al. [19] for the elution efficiency demonstrated by several eluents for Pd and Pt (i) 0.5 M thiourea in 1.0 M HCl: 100% elution efficiency for Pd; and (ii) 0.5 M NaClO4 in 1.0 M HCl: 70.9% elution efficiency for Pt, a solution containing 0.5 M thiourea and 0.5 M NaClO4 in 1 M HCl was initially prepared. The main objectives were to verify if it was possible to mixture all reagents (HCl, thiourea and NaClO4) in a single eluent without changing their elution efficiency, and if that same eluent would also enable Rh elution. However, the presence of the strong acid (HCl) and of the strong oxidizing agent (NaClO4) originated complexing agent (thiourea) instability, affecting the flow system operation (signals profile, sampling rate and results precision and accuracy). Therefore, this solution was considered inappropriate, and the two eluents described by Iglesias et al. [19] were then used separately. Differing from the previously described [19], the results obtained showed that 0.5 M thiourea in 1.0 M HCl resulted better than 0.5 M NaClO4 in 1.0 M HCl, even for Pt elution. However, it should be emphasized that, in this work, all the experiments were carried out in an on-line mode, while Iglesias et al. [19] performed their experiments in a batch mode, which can explain the observed differences, if some kinetic effect is present. Nevertheless, even allowing better results for Pt elution, 0.5 M thiourea in 1.0 M HCl was not the ideal eluent since it hindered the return to baseline of Pt analytical signal. It had also been tried to increase thiourea concentration but this resulted in impairment on the nebulisation due to the increase in the total dissolved solids. Complexing agents other than thiourea (L-cysteine, glycine and ammonium thiocyanate) were tested, varying the concentration and pH of their solutions, but the precision and accuracy of the results were always worse than those obtained when using 0.5 M thiourea in 1.0 M HCl. The use of a “simple aqueous” solution of 0.5 M thiourea (i.e., without 1.0 M HCl), was also tested, and it was verified an enhancement of the peak shape, i.e., the peak became more defined. This could probably be related both with an enhanced thiourea stability in aqueous solution and with an increased nebulisation efficiency (aqueous solutions are less viscous than acid solutions).

3.1.7.2. Eluent temperature. Another variable tested for the above mentioned eluent (0.5 M thiourea aqueous solution) was its temperature. It was concluded that the eluent heating to 100 °C led to an improvement both of the results precision and accuracy.

3.1.7.3. Eluent flow rate. When operating with on-line pre-concentration systems, the utilisation of eluents with a high desorption capacity and high eluent flow rates results in a sampling rate improvement. Nevertheless, taking into consideration the detection technique and the type of nebuliser that was being used in this work, the eluent flow rate should preferably not exceed 1.5 mL min⁻¹ [26]. Flow rate values ranging from 0.5 to 1.5 mL min⁻¹ were evaluated. The best results were obtained for 1 mL min⁻¹; lower and higher flow rates created plasma instability, thus affecting precision and accuracy.

When using Metalfix Chelamine of 40–80 μm particle size, Pohl et al. [10] considered the resin inappropriate for column operation, since it was prone to swelling or contracting due to differences in pH and ionic strength of the external and internal solutions in the resin bed. We did not observe these problems, i.e., the elution process was not significantly impaired by the use of an aqueous solution of thiourea as eluent.

3.1.8. Internal standardisation
In ICP-MS determinations, internal standards are used to monitor and correct any drift in sensitivity during the analytical run. For this purpose, ¹¹⁵In at a concentration of 1 μg L⁻¹ was added to the eluent. The influence that the mixing of thiourea and ¹¹⁵In solutions could exert over the PGEs determination was evaluated. This evaluation started with the individual registration of the signals obtained for PGEs and for ¹¹⁵In, i.e., two analytical cycles were performed; in the first cycle, a 0.1 μg L⁻¹ PGEs standard solution was passed through the column, and the elution of the PGEs retained was done only with the hot aqueous solution of 0.5 M thiourea; in the second cycle, the standard solution was replaced by a sample blank, and the elution was carried out using hot aqueous solution of 0.5 M thiourea plus ¹¹⁵In at a concentration of 1 μg L⁻¹. After these two analytical cycles, a third cycle was performed; this time the 0.1 μg L⁻¹ PGEs standard solution was passed through the column and the elution was carried out also using hot aqueous solution of 0.5 M thiourea plus ¹¹⁵In at a concentration of 1 μg L⁻¹. Results obtained in these experiments showed that the incorporation of the internal standard into the eluent did not affect either the PGEs or the ¹¹⁵In signals.

3.1.9. Post-elution washing step
The resin particles packed inside the column needed to be washed from the thiourea solution that still remained inside the flow system after the elution step—conditioning treatment. For this post-elution washing step different alternatives were tested: (i) air; (ii) blank solution; (iii) water followed by the blank solution; (iv) water; and (v) water followed by air. It was verified that the use of water, followed or not by air, led to a higher efficiency of the pre-concentration procedure. For all the other studied alternatives a diminishing of the resin’s affinity for PGEs was observed, resulting in a partial loss of the metals. The PGEs that were present in the first volume of sample loaded into the column during the pre-concentration step were not retained at the same extent when only air, the blank solution or water followed by the blank solution were used.

3.1.10. Co-existing metals
Since urine samples are highly complex matrices, it was important to verify the influence exerted by the co-existing metals on the affinity showed by Metalfix™ Chelamine™ for PGEs. For the effect, artificial urine was prepared [23] and several metals (Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn) were added, each one at a final concentration of 10 mg L⁻¹.
Urine “samples” were then prepared by spiking several 100 mL aliquots of the artificial urine with different amounts of PGEs (5–100 ng L\(^{-1}\)), and adding aqua regia to a final H\(^+\) concentration of 0.2 M. Calibration curves were obtained both for these “samples” and for the normal calibration standards. It was observed that, under the experimental conditions used, the tested metals did not influence PGEs retention by the resin, as it could be observed by the slope of the calibration curves obtained (Table 3).

### 3.2. Analytical features

Linear calibration plots for Rh, Pd and Pt up to 100 ng L\(^{-1}\) were obtained (Table 3). According to IUPAC recommendations [27], the LODs were calculated as the concentration corresponding to three times the standard deviation of 10 replicates of the blank, and were 1.2 ng L\(^{-1}\) (Rh), 0.4 ng L\(^{-1}\) (Pd) and 0.9 ng L\(^{-1}\) (Pt). The mean value obtained for the correlation coefficients of five calibration curves (\(n=7\)) were 0.9974 (Rh), 0.9985 (Pd) and 0.9979 (Pt).

### 3.2.1. Accuracy assessment: results of the recovery tests

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sample Initial Concentration</th>
<th>Concentration added</th>
<th>Concentration obtained</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Rh 0.9 ± 0.1</td>
<td>5</td>
<td>6.0 ± 0.3</td>
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<tr>
<td></td>
<td>Pd 1.01 ± 0.04</td>
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<td>20.0 ± 0.7</td>
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<tr>
<td></td>
<td>Pt 1.65 ± 0.09</td>
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<td>26 ± 1</td>
</tr>
<tr>
<td></td>
<td>Rh 1.2 ± 0.1</td>
<td>15</td>
<td>14.4 ± 0.4</td>
</tr>
<tr>
<td></td>
<td>Pd 2.43 ± 0.09</td>
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<td></td>
<td>Pt 5.4 ± 0.2</td>
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<tr>
<td></td>
<td>Rh 1.0 ± 0.1</td>
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<td></td>
<td>Pd 1.9 ± 0.06</td>
<td>35</td>
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<tr>
<td></td>
<td>Pt 0.88 ± 0.06</td>
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<tr>
<td>3</td>
<td>Rh 2.4 ± 0.2</td>
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<td></td>
<td>Pd 1.3 ± 0.1</td>
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<td>31.5 ± 0.6</td>
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<td>Pt 3.3 ± 0.06</td>
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<td>Rh 2.9 ± 0.1</td>
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<tr>
<td></td>
<td>Pd 0.96 ± 0.07</td>
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<tr>
<td>4</td>
<td>Pt 0.88 ± 0.04</td>
<td>60</td>
<td>5.4 ± 0.2</td>
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<tr>
<td></td>
<td>Rh 2.9 ± 0.1</td>
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<td>21.6 ± 0.5</td>
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<td>Pd 3.3 ± 0.1</td>
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<td>Pt 2.9 ± 0.1</td>
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<td>19 ± 2</td>
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<td>5</td>
<td>Rh 1.2 ± 0.1</td>
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<td></td>
<td>Pd 0.96 ± 0.07</td>
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<td>18.3 ± 0.5</td>
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<tr>
<td></td>
<td>Pt 4.3 ± 0.2</td>
<td>60</td>
<td>79 ± 1</td>
</tr>
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</table>

Results (ng L\(^{-1}\)) expressed as mean ± S.D. (\(n=3\)); sample volume = 10 mL; flow rate = 4 mL min\(^{-1}\); eluent volume = 2 mL; flow rate = 1 mL min\(^{-1}\).
Accuracy assessment involved the analysis of urine samples \((n=5)\) before and after the addition (made previously to samples microwave digestion) of small volumes of a standard solution (Table 4). The obtained recovery values ranged between 89% and 105% for Rh; 90% and 104% for Pd; and 93% and 105% for Pt, showing that the developed analytical flow system presented adequate accuracy for this analytical purpose.

4. Conclusions

The proposed flow system proved to be a simple way to overpass the problems related with the Q-ICP-MS determination of PGEs in highly complex matrices. During the pre-concentration step, it allowed the elimination of the interfering metals, thus preventing the formation of atomic and molecular ions that might interfere with PGEs determination. Furthermore, it allowed PGEs pre-concentration, making possible its determination at very low concentration. Since there is an increasing interest in PGEs determination in biological samples, the proposed flow system may represent an important contribution for PGEs determination not only in urine but also in other equally complex matrices, such as acid digests of biopsy/autopsy materials.

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References