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Improved voltammetric method for simultaneous determination of Pt and Rh using second derivative signal transformation – application to environmental samples

Carlos E. Monteiro^{a,b,*}, Antonio Cobelo-Garcia^c, Miguel Caetano^b, Margarida M. Correia dos Santos^{a*}

^aCentro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais 1, 1049-001, Lisboa, Portugal

^bIPMA—Portuguese Institute of Sea and Atmosphere, Division of Environmental Oceanography and Bioprospection, Av. Brasília, 1449-006 Lisbon, Portugal

^cBioxeoquímica Mariña, Instituto de Investigacións Mariñas IIM-CSIC, Eduardo Cabello 6, 36208 Vigo, Pontevedra, Spain

cessmonteiro@gmail.pt

mcsantos@tecnico.ulisboa.pt

*Corresponding authors: Carlos E. Monteiro, Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais 1, Torre Sul Lab 11.6-2, 1049-001, Lisboa, Portugal, +351 218 419 177

*Corresponding authors: Margarida M. Correia dos Santos, Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais 1, Torre Sul 11.6-6, 1049-001, Lisboa, Portugal, +351 218 419 272

Abstract

The determination of Platinum-group elements (PGE) in relevant environmental matrices is a challenging task. Sensitive and accurate analytical procedures for simultaneous determination of Pt and Rh are still needed. In this study, we report for the first time on the use of second derivative signal transformation to the ultra-trace simultaneous determination of Pt and Rh by Adsorptive Cathodic Stripping Voltammetry (AdCSV). With that step, the ill-defined peaks typically observed in the original voltammograms are transformed into well-shaped peaks, resulting in accurate detection. The experimental conditions were investigated and optimised: a suitable electrolyte for both elements, with less reagents consumption, (0.25 M H₂SO₄, 0.05 M HCl, 0.01 M FA and 0.5 mM HZ), deposition time (t_d) and deposition potential (E_d). For $t_d = 120$ s and $E_d = -0.75$ V, linear relationships $r > 0.999$ were obtained in the concentration range up to 5.8 ng L⁻¹ (27 pM) for Pt and up to 3.4 ng L⁻¹ (34 pM) for Rh. Limits of detection were 0.2 ng L⁻¹ for Pt and 0.08 ng L⁻¹ for Rh. Lower values can be achieved by increasing the deposition time. Limits of quantification, LOQ, calculated as 3 times LOD, were 0.5 ng L⁻¹ for Pt and 0.2 ng L⁻¹ for Rh. The sensitivity of Pt was affected by elevated Zn concentrations, whereas a minor effect was observed for Rh. However, Pt and Rh determinations were not influenced using the standard addition method. Precision as intermediate precision and expressed as relative standard deviation, based on Pt and Rh spiked solutions and digested road dust CRM BCR-723 was 17 % and 20 % for Pt and Rh, respectively. Recoveries of CRM were around 90 % for both elements. The method was successfully applied in the simultaneous determination of Pt and Rh in sediments from Tagus estuary and, for the first time, dissolved Rh was determined in water samples of a waste water treatment plant. Application of this technique in a multidisciplinary approach will be a relevant contribution to the current understanding of PGE cycle and fate in the environment.

Keywords: Platinum, Rhodium, Simultaneous determination, Adsorptive voltammetry, Second derivative, Environmental samples

1. Introduction

Platinum-group elements (PGE) constitute a group of rare and noble elements which includes platinum (Pt), palladium (Pd), rhodium (Rh), iridium (Ir), osmium (Os) and ruthenium (Ru). PGE are severely depleted in the earth's crust: 0.4 ng g^{-1} for Pt and Pd; 0.1 ng g^{-1} for Ru; 0.06 ng g^{-1} for Rh; and 0.05 ng g^{-1} for Ir and Os [1]; [2]. Yet they have been increasingly explored and used over the past decades in several applications due to their physical and chemical properties [3]. The automobile industry is the main sector responsible for the PGE global demand, representing approximately 45 % Pt, 50 % Pd and 5 % Rh in 2016 [4]. This is mostly due to the use of PGE in automobile catalytic converters to reduce the emissions of other pollutants, carbon monoxide, nitrogen oxides and hydrocarbon [2]. As a result, anthropogenic emissions of PGE have grown significantly over the last decade [5]. Particles released from catalytic converters due to abrasion or degradation result in widespread distribution of PGE, mainly near high traffic roads [6]. Thus, accumulation of PGE has been observed in sediments and vegetation, exceeding largely the natural background levels [5]; [6]. As to platinum and rhodium in aquatic systems, Pt(II), Pt(IV) and Rh(III) are the most important oxidation states, depending on salinity and redox conditions [7]; [8]. Inorganic speciation is dominated by aquo-hydroxo, aquo-chloro and mixed aquo-hydroxo-chloro complexes [7]; [8]. Furthermore, there is evidence of Pt and Rh interaction with organic matter,

which may be a key parameter in speciation and distribution of PGE in aquatic ecosystems [8]; [9].

Platinum has received the utmost attention among the PGE studies. More recently, Rh in environmental samples has been reckoned, but only with emphasis on urban and roadside solid samples. Thus, data on its total dissolved concentrations still lacks [5], and Rh speciation studies are scarce (e.g. [8]). The improvement of analytical techniques over the past few decades, such as electrothermal atomic absorption spectrometry (ET-AAS) and inductively coupled plasma mass spectrometry (ICP-MS), allowed the individual and simultaneous determination of those elements in different environmental matrices [5]. Despite the high sensitivity of ICP-MS for PGE analysis it has some disadvantages, such as the need of matrix separation due to polyatomic interferences from other elements [10]. Overall, this is an expensive technique, as well as time-consuming, and susceptible of cross-contamination.

Voltammetric techniques provide a simple and sensitive way to directly determine Pt and Rh at ultra-trace levels. Additionally, it is less expensive and appears adequate for routine analysis [5]; [11]. Several electroanalytical procedures have been reported mostly based on adsorptive cathodic stripping voltammetry (AdCSV) on a mercury electrode. Although alternative electrodes have been investigated envisaging a similar analytical performance to mercury [12]; [13], detection and quantification limits reported are insufficient to study the behavior of PGEs in unspoiled environments, particularly in the case of Rh [1].

Platinum-group elements can form highly stable complexes which can act as catalysts for hydrogen production after metal reduction on a mercury electrode [14]. In the case of Pt, the surface active complex mostly explored is that with formazone, produced *in situ* from the reaction of formaldehyde (FA) and hydrazine (HZ) [11]; [15]; [16]; [17].

The surface active complex adsorbs on the mercury electrode and the catalytic-promoted hydrogen reduction occurs in acidic (e.g. H_2SO_4) conditions due to the formation of $\text{Pt}(0)$ at the electrode surface, giving rise to a catalytic wave upon metal reduction. Furthermore, the catalytic behaviour of $\text{Pt}(\text{IV})$ is similar to $\text{Pt}(\text{II})$, since hydrazine can quantitatively reduce $\text{Pt}(\text{IV})$ to $\text{Pt}(\text{II})$ [18]. Alternative methods using other ligands were described, and found comparable with those employing formazone [19]. In the case of Rh, catalytic waves in formaldehyde–HCl media have been reported and the nature of the surface active complexes may well be chloro-complexes and/or formaldehyde complexes [8]; [20]; [21].

The pioneer works of Zhao and Freiser [18] and van den Berg and Jacinto [15] established the ultra-trace individual determination of Pt, while Wang and Taha [22] and Hong et al. [20] have set up a methodology for Rh. Other works dealing with environmental samples followed, prevalently addressing Pt [5]. Another challenge has been the simultaneous determination of Pt and Rh in real environmental samples and some applications were reported [11]; [16]. Various supporting electrolytes and different complexing agents have been used and although in most works an optimised procedure is presented, in some cases the nature of the surface active complexes for rhodium remains elusive [20]; [23].

In most of the works, voltammetric peak currents were used for quantification, which can have a drawback. One disadvantage is the intense background current or interfering peaks that affects the target signal, causing ill-defined peaks influencing the accuracy of measurements [17]. At ultra-trace concentrations, Pt and in particular Rh peak currents may be almost imperceptible. An improvement was achieved on the individual determination of Pt and Rh using second derivative signal transformation, as reported by Cobelo-García et al. [17] and Almecija et al. [21], respectively. Low background

interferences due to current noise or matrix elements were better discriminated, as well-defined peaks and low LOD were achieved using signal transformation.

We hypothesized that (1) the use of second derivative signal transformation improve the simultaneous analysis of Pt and Rh by AdCSV in a single scan. Simultaneous analysis of both elements will (2) reduce the cost of reagents used during the analytical procedure, being the method more environmentally friendly, and (3) reduce the time of analysis, making it appropriate for routine analysis. Therefore, in this study we report the optimised conditions (electrolyte composition and instrumental parameters) for the simultaneous analysis of Pt and Rh by AdCSV using the second derivative signal transformation in the voltammograms.

The suitability of the method to real environmental matrices is well demonstrated by its application to Pt and Rh determinations in sediments from Tagus estuary and water samples from an urban waste water treatment plant (WWTP).

2. Material and methods

2.1. Material and Chemicals

Laboratory material was previously acid-cleaned with immersion in ~20 % nitric acid (HNO_3) and hydrochloric acid (HCl) baths for at least 48 hours. Afterwards, all material was rinsed with Milli-Q water ($18.2 \text{ M}\Omega \text{ cm}$, 25°C) and let to dry in a clean room. All reagents used in analysis and samples digestion were of high-purity grade: sulphuric acid (H_2SO_4) $\geq 95 \%$ (*TraceSELECT*, Fluka), HNO_3 65 % and HCl 30 % (*Suprapur*, Merck), formaldehyde 13 M (FA 36.5 %, Riedel-de-Haen), hydrazine sulphate (HZ; p.a., Fluka), and hydrogen peroxide (H_2O_2) 30 % (p.a., ACS ISO, Emsure). Solutions of 0.53 M FA and 50 mM HZ were prepared in Milli-Q water and stored in

perfluoroalkoxy (PFA) flasks. These solutions are stable for several weeks [17]. Standard solutions 1000 mg L⁻¹ (*TraceCERT*, Fluka) of Pt and Rh were used to prepare daily diluted standard solutions of 1.0 µg L⁻¹ Pt in 1M HCl and 1.0 µg L⁻¹ Rh in 0.1M HCl. The electrolyte final concentrations in the voltammetric cell were 0.25 M H₂SO₄, 0.05 M HCl, 0.01 M FA and 0.5 mM HZ.

2.2. Apparatus and analysis

Voltammetric determinations were performed in an Autolab PGSTAT 128N (Metrohm) coupled to a polarographic stand model 663 VA (Metrohm). Parameters of the equipment and data acquisition were controlled with GPES v. 4.9 software (EchoChemie). All measurements were performed in triplicate under clean and acclimatised conditions (25 ± 2 °C). The stand was equipped with a static mercury drop electrode (SDME) as working electrode, a Ag/AgCl as reference electrode, placed inside a salt bridge with saturated KCl (3 M) and a glassy carbon rod as counter electrode. Polytetrafluoroethylene (PTFE) vessels were used as voltammetric cells in all experiments.

For the voltammetric analysis, after purging with N₂ for 10 minutes prior to the measurements and homogenization using a rotating PTFE rod, at 3000 rpm, a new mercury drop was extruded. While stirring, a deposition potential $E_d = -0.75$ V was applied for the deposition time $t_d = 120$ s (or $t_d = 300$ s) (see section **3.2 Optimisation of the conditions**). Afterwards, 10 s of quiescence period was given. Then, a stripping scan was performed using differential pulse (DP) mode from -0.7 to -1.2 V, at a scan rate of 20 mV s⁻¹ with modulation time of 0.04 s and amplitude of 25 mV, an interval time of 0.2 s and step potential of 4 mV. Total Pt and Rh were quantified using the standard addition method.

2.3. Procedure for Pt and Rh digestion in sediments and CRM

Sediments and certified reference material (CRM) were ashed in quartz crucibles at 800 °C following the heating scheme of Nygren et al. [24] to remove the organic matter that interferes with the voltammetric determination. The residue was transferred to PTFE vessels and digested using a mixture of concentrated acids (3 mL HCl and 1 mL HNO₃) at 195 °C for 4 hours in a hot plate. After cooling, the caps were removed from the vessels and samples were allowed to evaporate the acids near dryness at 85 °C. Samples were then re-dissolved in 1 mL of H₂SO₄ and the remaining HCl and HNO₃ were left to evaporate to a constant volume. The residue was transferred to polypropylene (PP) Digitubes (SCP Science) and diluted to 25 mL with 0.1 M HCl following the procedures previously described [7]; [17]; [21].

2.4. Procedure for Pt and Rh analysis in waters

Water samples from an urban WWTP were collected and stored in acid-washed PP bottles (Nalgene). Samples were filtered using acid-cleaned 0.2 µm polycarbonate (PC) membranes (Millipore). Filtered samples were immediately acidified with concentrated HCl (Suprapur, Merck) to pH ≈ 1.0. Previously to the voltammetric analysis, the water samples were UV digested under a 125 W high-pressure mercury lamp (Osram) for 3 hours [25]. This step removes the dissolved organic content, which causes interferences in the voltammetric determination. To assure rapid and complete degradation of organic matter, 1 µL of concentrated H₂O₂ per 1 mL of sample was added into the digestion quartz tube [26].

2.5. Data processing

Using the GPES v4.9 software the original voltammograms were processed as described by Cobelo-García et al. [17] and Almecija et al. [21]. To the original voltammogram

was applied a smoothing step by a factor of 2, according to the Savitsky-Golay (SG) algorithm, which removes noise signals that could be intensified after the double derivation step. Then, the second derivative signal transformation (2nd Der) was obtained by applying twice the derivative transformation, expressed as:

$$\frac{dy}{dx} \approx 0.5 \left(\frac{y(n)-y(n-1)}{x(n)-x(n-1)} \right) + 0.5 \left(\frac{y(n+1)-y(n)}{x(n+1)-x(n)} \right) \quad (1)$$

where $y = I$ and $x = E$ corresponding to the current intensity (in A) and applied potential (in V), respectively, and n indicates the number of data points. This procedure removed very efficiently background interferences while keeping good peak-shaped transformed signals. After signal transformation, each metal peak height was measured based on peak–peak linear baseline, which has been proven to provide the most accurate results for Pt (Cobelo, 2014) and for Rh (Almecija, 2016).

Additionally, the necessary statistical analysis and graphical representations were performed with the open source language R and the available packages [27].

2.6. Samples from the Tagus Estuary River and WWTP

To apply our optimised method we have chosen different environmental samples to monitor PGE levels. Superficial sediments were collected in the Tagus estuary nearby an industrial area in early June 2016. Additionally, water was collected in a WWTP of Lisbon (Portugal). Two water samples were collected (inflow and outflow of the WWTP) after a long dry period, just before raining, and soon after the first intense rainfall in early October 2016.

3. Results and Discussion

3.1. Second derivative transformation

Several parameters were investigated to optimise the procedure for simultaneous determination of Pt and Rh by means of AdCSV using the second derivative (2nd Der) signal transformation (see section 3.2 *Optimisation of the conditions*). In addition to the electrolyte composition, working conditions like equilibration time, deposition potential and deposition time, were assessed and optimised. Possible interferences, mainly from electrochemical signals close to the analytical signals of Pt and Rh, were also investigated.

Figure 1a shows the original voltammograms obtained in the optimised conditions of an aliquot of digested road dust CRM BCR-723 (100 μ L of sample digest in 15 mL) corresponding to 3.0 ng L⁻¹ Pt and 0.47 ng L⁻¹ Rh, and two standard additions of 1.0 ng L⁻¹ Pt and 0.33 ng L⁻¹ Rh. Ill-defined peaks were observed for Pt, around -0.89 V, and especially for Rh where a broad shoulder is barely seen, at potentials close to -1.11 V, superimposed by the high background current. Signals like these are difficult to measure and thus often lack the necessary accuracy. The use of the 2nd Der transformation, showed in Fig. 1b, provided well-defined peaks for both metals, which were easily measured and diminished the errors associated with this step.

3.2. Optimisation of the conditions

3.2.1. Electrolyte composition

For Pt determination by AdCSV, previous studies have taken advantage of the well-established complex with formazone, produced *in situ* by the reaction of HZ with FA [15]; [16]; [17]; [23]. Formazone was also referred as the ligand for Rh determination

by AdCSV [23]. In HCl media and in the presence of FA, the Rh surface active complexes are supposed to be a mixture of complexes with FA and chloro-complexes [20]; [21]. In any case, high acid concentration is needed in the electrolyte to obtain a catalytic hydrogen current and H_2SO_4 and/or HCl have been used.

To achieve the optimum procedure, we explored the nature of the surface active complexes in hydrazine + formaldehyde and the acids media to be used for the simultaneous determination of Pt and Rh. The concentrations of 10 mM FA and 0.5 mM HZ followed our previous experience in the individual determination of Pt and Rh [17]; [21]. As to the effect of the acids, various mixtures of HCl and H_2SO_4 were prepared. Figure 2a shows the influence of H_2SO_4 concentration on 2.0 ng L^{-1} Pt and 0.67 ng L^{-1} Rh signals while keeping the HCl concentration constant (0.4 M [21]). Sensitivity of Rh slightly decreased for H_2SO_4 concentrations higher than 0.25 M and Pt sensitivity above 0.4 M. A compromise for the H_2SO_4 concentration was 0.25 M. As to the influence of the HCl concentration on the voltammetric signals at constant H_2SO_4 concentration (0.5 M [17]), Fig. 2b shows that the sensitivity for both Rh and Pt is less dependent on the HCl concentration, in opposition to previous reports, e.g. [16]; [23]. The sensitivity obtained in the absence of HCl does not differ, within the experimental errors, from that in the presence of HCl up to 0.5 M HCl. Therefore, Rh chloro-complexes are not relevant surface active complexes in H_2SO_4 , 0.01 M FA and 0.5 mM HZ medium and HCl can be removed from the electrolyte. Because HCl is present in some samples due to the conditions used for sample preparation, as previously described, a concentration of 0.05M HCl was set in the voltammetric cell in all experiments.

The nature of Rh surface active complexes was assessed by adding formaldehyde followed by hydrazine to 0.25 M H_2SO_4 electrolyte and in the presence of 2.0 ng L^{-1} Pt and 0.67 ng L^{-1} Rh. The voltammetric signal of Rh was immediately observed after FA

addition and its characteristics (intensity and potential) did not change upon HZ addition (S.I. Fig. S1). Only in the presence of both FA and HZ, with formazone being produced *in situ*, was observed the Pt signal, while Rh characteristics kept stable within the experimental error. Accordingly, Pt adsorbs on the electrode surface as the Pt-formazone complex, as expected, while the surface active complex in the case of Rh is that with formaldehyde (S.I. Fig. S1).

3.2.2. *Equilibration Time*

After the addition of all reagents in the voltammetric cell, the effect of equilibration time on the signal of Pt and Rh was tested from 10 to 30 minutes while stirring. No detectable differences were found by varying the equilibration time prior to the analysis for Rh signal. The same occurred with Pt signal. Therefore an equilibration time of 10 minutes (coincident with the purging and stirring period) was used in all experiments.

3.2.3. *Deposition Potential and Deposition Time*

For the most convenient deposition potential for Pt and Rh determination, previous works referred $E_d = -0.3$ V and $E_d = -0.7$ V as more favourable for Pt [17] and Rh determination [21], respectively. Consequently, in this work E_d was varied between 0 V and -1.1 V for a deposition time (t_d) of 120 s (Fig. 3).

The sensitivity for Pt was almost constant between -0.1 and -0.85 V, decreasing abruptly at more negative potentials due to Pt reduction. Otherwise, the sensitivity for Rh tended to increase with the more negative potential. Therefore, -0.75 V was selected as a suitable deposition potential for the simultaneous determination of Pt and Rh. When the concentration of Pt is low compared to Rh, it is possible to use a more positive deposition potential (e.g. -0.3 V [17]) where the adsorption of the rhodium complex is less favourable. However, this is not found in most environmental matrices,

where higher Pt concentrations than Rh are expected (up to 10-fold [28]). So, a pre-accumulation at the more favourable potential for Rh is desirable.

The influence of deposition time on the analytical signal, peak heights measured using the second derivative transformation, was also investigated for Pt and Rh solutions at two different levels of concentration (Fig. 4): a) 2.0 and 4.0 ng L⁻¹ Pt; and b) 0.66 and 1.3 ng L⁻¹ Rh. Linear relationships with correlation coefficients > 0.999 were obtained for deposition times up to 300 s. Also in Fig. 4 can be observed that saturation of the electrode surface does not occur in this range of concentrations either for Pt or Rh. The choice of the optimum t_d value will be dependent on the concentration of the analyte to be determined. Accumulation times of 120 s proved to be adequate for the determination of Pt and Rh in relevant environmental matrices, such as sediments and road dust CRM BCR-723. However, in water samples these metals tend to be present in lower concentrations. Thus, the deposition time should be increased in order to attain an accurate separation of Pt and Rh signals from background values.

The optimised conditions for the simultaneous determination of Pt and Rh using the second derivative are given in Table 1.

3.3. Interferences

Interferences in voltammograms can be due either to the presence of surface active compounds or interfering peaks. The effect of surface active compounds can be quite serious and that is why samples are previously treated, e.g. in order to destroy all organic matter. Other interferences could be due to the formation of other metal complexes with formazone. However, these complexes were reported as negligible for metal ions such as Fe and Cu [15]; [16]. Contrarily, the existence of elevated concentrations of Zn in samples may be problematic, because Zn can be reduced at a

mercury electrode in the potential range between the Pt and Rh signals. Consequently, we examined Zn interferences in the simultaneous determination of Pt and Rh in solutions containing 1.0 ng L^{-1} Pt and 0.33 ng L^{-1} Rh, while varying the Zn concentration (Fig. 5). When compared to the Pt and Rh signals without Zn in solution (Fig. 5a), the signal intensity of Rh was not immediately affected in the range of Zn concentrations analysed, while there was a decrease of the signal intensity for Pt at Zn concentrations higher than 0.7 mg L^{-1} ($\sim 11 \text{ }\mu\text{M}$) (Fig. 5b). This decrease may not be immediately detected in the original voltammogram (Fig. 5c). Instead, a broad shoulder between Pt and Rh stripping potentials appears with the increase of Zn concentration causing distortion, in particular to the Pt signal. The use of 2nd Der transformation improved the ill-defined peaks, evidencing how the Pt signal is more affected than that of Rh by the presence of Zn in solution (Fig. 5d). Platinum and Rh determination by the standard addition method were not affected in the presence of at least 2 mg L^{-1} Zn, regardless of the decreasing sensitivity for Pt. This result is in line with those previously reported, having maximum tolerable of $2 - 3 \text{ mg L}^{-1}$ [16] or 10 mg L^{-1} [23]. If it is considered the Zn concentrations found in salt marsh sediments colonized by vascular plants, which typically retain very high levels in their root tissues, it is possible to estimate a Zn concentration value in the voltammetric cell. Santos-Echeandía et al. [29] found up to $6000 \text{ }\mu\text{g g}^{-1}$ of Zn in the roots of salt marsh plants and $2500 \text{ }\mu\text{g g}^{-1}$ of Zn in sediments of the Tagus estuary, in SW Europe. Considering the amount of sample used for acid digestion (0.2 g), their final volume (25 mL), the frequent aliquot used for Pt and Rh analysis (1 mL) and the volume in the voltammetric cell (15 mL), then the concentration of Zn will be 3.2 mg L^{-1} for the roots sample and 1.3 mg L^{-1} Zn for the sediment. In sediments, typical concentrations of Zn are lower than $700 \text{ }\mu\text{g g}^{-1}$ [30]; [31], and this does not represent concern. Additionally, Zn concentrations in waters are

usually much lower (tens of $\mu\text{g L}^{-1}$) than those in sediments and should not constitute a problem. It is noteworthy the potential Zn contamination and interference when analysing Pt and Rh. Thus, depending on the degree of Zn contamination, this metal should be also monitored.

3.4. Characteristics of the Analytical Procedure

Very good linear calibration curves ($r > 0.999$) were obtained in the concentration range up to 5.2 ng L^{-1} Pt and 3.5 ng L^{-1} Rh in the optimised conditions (S.I. Fig. S2). Limits of detection (LOD) were calculated as 3 times the standard deviation of the blank and also from $\text{LOD} = 3S_{x/y}/m$ ($S_{x/y}$ is the standard error of the calibration curve and m the slope of the calibration curve [32]). Similar values of LOD were obtained using both approaches, and only the latter is presented in Table 2. The average values of LOD were 0.2 ng L^{-1} for Pt and 0.08 ng L^{-1} for Rh ($n > 10$). Lower values can be achieved increasing the deposition time. Limits of quantification, LOQ, were calculated as 3 times LOD (Table 2) and were 0.5 ng L^{-1} for Pt and 0.2 ng L^{-1} for Rh ($n > 10$). The sensitivity of the method was assessed by the slope of calibration curves obtained for reagent blanks ($n > 10$), recovery solutions ($n = 5$) and CRM BCR-723 ($n = 7$), showed in Table 2.

Intermediate precision of voltammetric determinations with the optimised method, expressed as RSD, was calculated based on Pt and Rh spiked solutions ($n = 5$) and the digested CRM (road dust BCR-723, $n = 7$) comparing the results obtained on different days using the same instrument. Statistical analysis was performed to check the data for outliers. The values are shown in Table 2 and are similar to those previously reported in Pt and Rh determination [21]; [23].

3.5. Application of the method to estuarine sediments and water samples

After the optimisation of the method for the simultaneous determination of Pt and Rh, it was applied to environmental samples: estuarine sediments (#A and #B) from the Tagus estuary, and water samples from an urban WWTP collected after a dry period and soon after the first heavy rains.

The accuracy of the determination was assessed using the CRM road dust BCR-723. The transformation of the original signal by using the 2nd Der clearly improved the ill-defined peaks originally observed, especially in the case of Rh. As depicted in Fig. 1, the voltammograms for the road dust CRM BCR-723 showed well-defined peaks after the second derivative transformation, and in particular for Rh the accuracy of the measurements increased. Recoveries around 90 % for Pt and Rh were obtained in BCR-723 digested samples using the digestion procedure previously described for Pt [17]. In addition, these results confirm that the procedure used for Pt extraction is also suitable for the extraction of Rh in solid matrices [21]. With the spiked solutions, recoveries were higher than 95 % for both elements (Table 3). In Fig. 6 is now shown for sediment #B a complete set of standard additions using the 2nd derivative voltammograms (Fig. 6a), and the corresponding calibration plot (Fig. 6b) illustrating the powerfulness of the technique.

In the sediments from the Tagus estuary the concentrations of Pt and Rh in sample #A were $3.50 \pm 0.03 \text{ ng g}^{-1}$ and $0.14 \pm 0.04 \text{ ng g}^{-1}$, respectively, while in sample #B the concentrations were $6.8 \pm 0.9 \text{ ng g}^{-1}$ of Pt and $0.53 \pm 0.08 \text{ ng g}^{-1}$ of Rh (Table 3). These values clearly highlight an enrichment of up to 10-fold of Pt and Rh in bed sediments when compared to Pt background concentration in Tagus estuary [33] and to natural crustal abundance of Rh [1]. The high levels of Pt and Rh may have resulted from emissions of automotive catalytic converters since 1990s [34]. Assessment of Pt and Rh sources to the different environmental matrices are frequently discussed in terms of

Pt/Rh concentration ratios [35]. The ratio calculated for the bed sediment #A was 25 and for #B was 13, which clearly evidences the anthropogenic pressure, and being #B within the range of values typically found for three-way catalytic converters (4 – 16; [34]). The Pt/Rh ratio often shows high variability depending on the type of sample, on its preparation and/or analysis procedures. Therefore, it is difficult to compare data. However, it has been suggested that high variability of Pt/Rh in sediments is explained by different sources, namely industrial or hospital effluents where distinct signatures may be identified [38], than by the changes in actual PGE ratio in the composition of automotive three-way catalytic converters [36], which nowadays are commonly used. Sediment #A was in the surroundings of an industrialised area, which could explain higher Pt/Rh than in #B. Furthermore, chemical processes may differently affect Pt and Rh causing higher ratio variability.

In the determination of Pt and Rh in WWTP water samples, a longer accumulation time was used: $t_d = 300$ s. It is noteworthy that increasing the deposition time allowed the clear separation of metal signal in the samples from the background wave (blanks) using the 2nd Der step. This was especially evident in the case of Rh. Lower LOD are also obtained, of 0.05 ng L^{-1} and 0.04 ng L^{-1} for Pt and Rh, respectively. Pt concentrations of $5.0 \pm 0.7 \text{ ng L}^{-1}$ to $16 \pm 2 \text{ ng L}^{-1}$ were determined in the outflow and inflow samples, respectively, collected after a period of dry weather. Samples collected soon after the first rains depicted higher Pt concentrations, of $10.4 \pm 0.3 \text{ ng L}^{-1}$ to $25 \pm 2 \text{ ng L}^{-1}$ in the outflow and inflow samples, respectively. In the case of Rh, the concentrations determined either in the inflow or outflow samples, collected before and soon after the rainfall, were similar within the experimental errors, averaging $0.21 \pm 0.05 \text{ ng L}^{-1}$ (Table 3). Dissolved Pt and Rh concentrations determined in WWTP samples also reflect the anthropogenic pressure, with Pt levels intensified after the first rains as previously

reported in Europe [37]. Published data on dissolved concentrations of Rh in environmental samples are scarce, either due to the type of sample analysed or the high LOD of the techniques used. To the best of our knowledge, these are the first values reported for a WWTP and one of the few published for waters [28]. Moreover, these results prove well the advantage of the low cost, sensitive and reliable voltammetric technique here optimised. The Pt/Rh ratio is usually applied to soils and sediments and was never reported for water samples, perhaps due to the absence of dissolved Rh values. In the water samples from the WWTP elevated ratios were found reaching 147 in the inflow water soon after the rain, although decreasing to 53 in the outflow water. Additional research is needed to evaluate the relationship between these values and the published ones for soils and sediments. Further research is ongoing to fully characterise PGE distribution within the Tagus estuary.

4. Final remarks

A method for the simultaneous determination of Pt and Rh by Adsorptive Cathodic Stripping Voltammetry using second derivative of the voltammograms was optimised and successfully applied to relevant environmental samples. At ultra-trace concentrations ill-defined peaks are usually observed and the use of the second derivative transformation improves the Pt and in particular Rh signals. In addition, reagents consumption and time of analysis were also optimised in the analytical procedure. Less reagents were needed and the overall time of analysis reduced.

Comparable LOD were achieved as for the individual determination of Pt or Rh, being appropriate for environmental matrices. Intermediate precision of the method, expressed as RSD, was also within the acceptable values for determinations at ultra-trace levels.

Recoveries were around 90% for both Pt and Rh using CRM BCR-723 and evidenced the accuracy of the procedure. The application to relevant environmental samples indicated that the method is suitable for the analytical quantification of Pt and Rh, reducing the costs and time by the simultaneous determination and making the method attractive for routine analysis. Longer deposition times can be used to accurately separate the metals signal from background voltammograms at lower concentrations. To the best of our knowledge, dissolved Rh concentrations in water samples of WWTP are reported for the first time.

The method here developed and validated offers the high resolution necessary to measure the low signals frequently observed in low contaminated environmental samples, therefore improve the accuracy of Pt and in particular Rh concentrations determined in pristine environments. Thus, application of this technique in a multidisciplinary approach may be a relevant contribute, giving rise to the current understanding of these elements cycle and fate in the environment.

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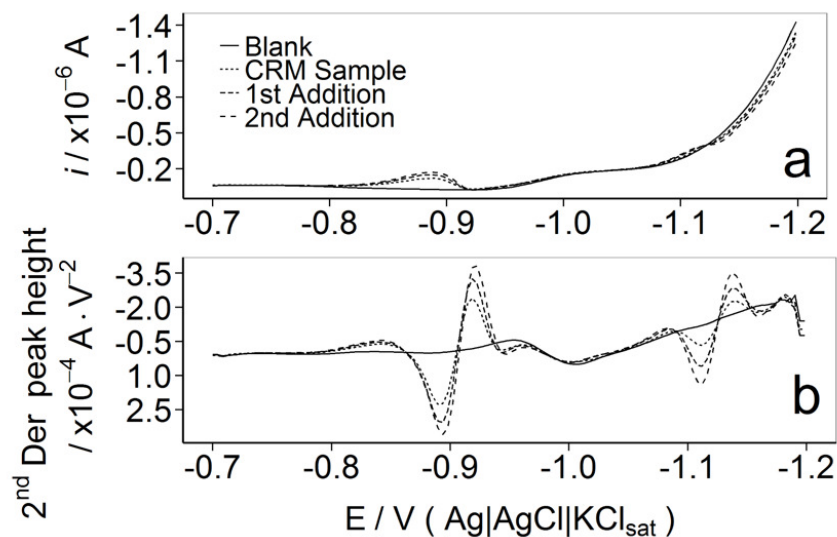


Figure 1 – (a) Original and (b) second derivative (2^{nd} Der) voltammograms of road dust CRM BCR-723, obtained in the optimised conditions: 1) blank (solid line); 2) CRM sample BCR-723 (100 μL of sample digest in 15 mL) corresponding to 3.0 ng L^{-1} Pt and 0.47 ng L^{-1} Rh (small dotted line); 3) first standard addition (dotted line), 1.0 ng L^{-1} Pt and 0.33 ng L^{-1} Rh; and 4) second standard addition (long dotted line), 2.0 ng L^{-1} Pt and 0.67 ng L^{-1} Rh. $t_d = 120 \text{ s}$ and $E_d = -0.75 \text{ V}$. Electrolyte: $0.25 \text{ M H}_2\text{SO}_4$, 0.05 M HCl , 0.01 M FA and 0.5 mM HZ .

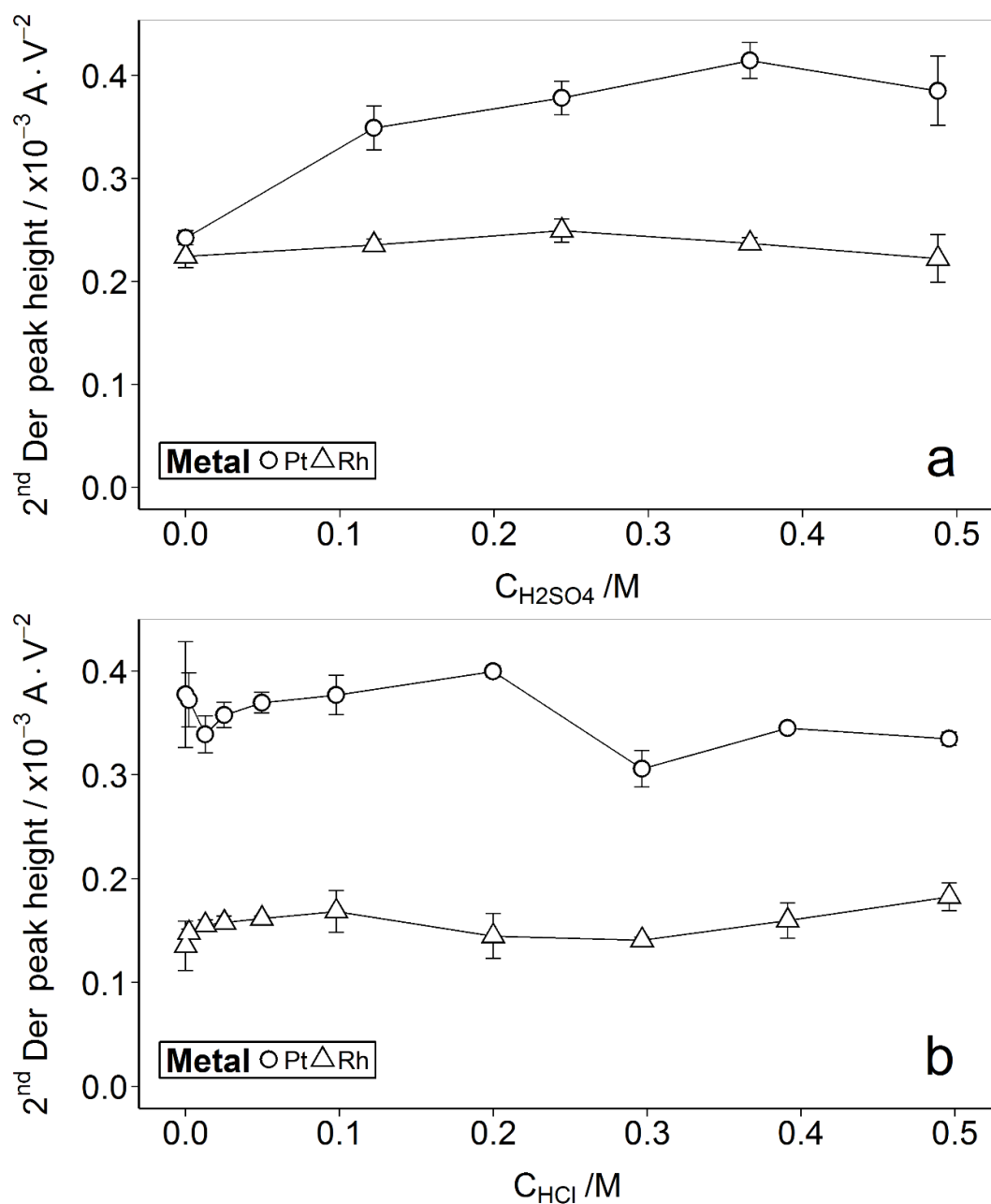


Figure 2 – Second derivative (2^{nd} Der) peak heights of 2.0 ng L^{-1} Pt (circles) and 0.67 ng L^{-1} Rh (triangles) with (a) variation of H_2SO_4 concentration in 0.4 M HCl and (b) variation of HCl concentration in 0.5 M H_2SO_4 . Electrolyte: 0.01 M FA and 0.5 mM HZ; deposition times: $t_d^1 = 120 \text{ s}$ and $t_d^2 = 60 \text{ s}$; deposition potentials: $E_d^1 = -0.3 \text{ V}$ and $E_d^2 = -0.7 \text{ V}$.

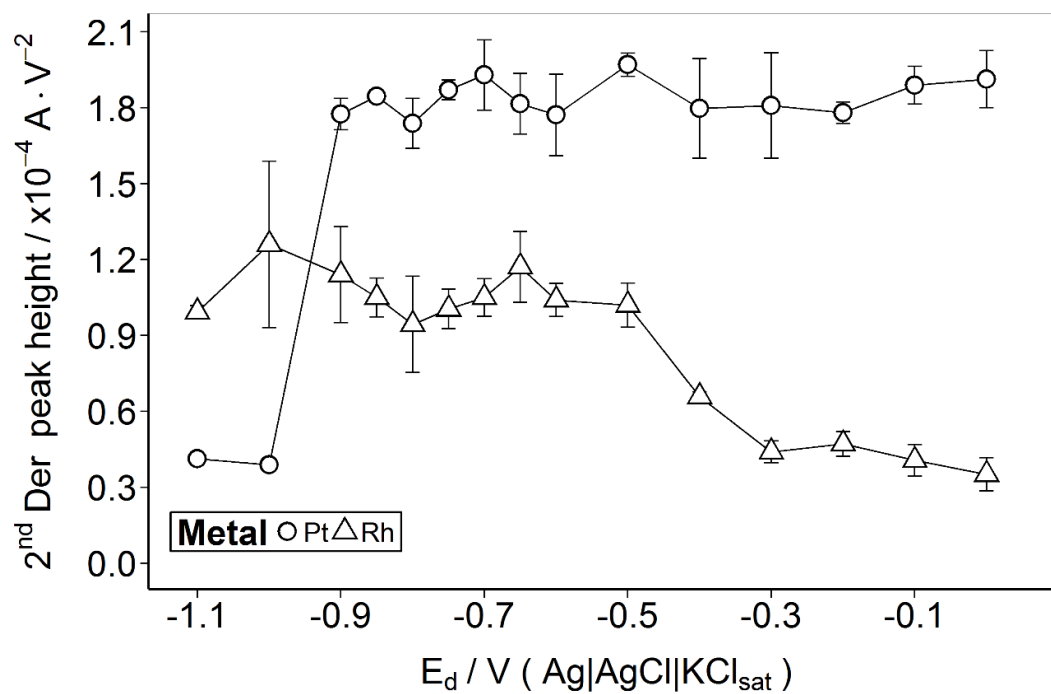


Figure 3 – Second derivative (2nd Der) peak heights of 1.0 ng L⁻¹ Pt (circles) and 0.36 ng L⁻¹ Rh (triangles) with variation of deposition potentials, E_d ; $t_d = 120$ s. Electrolyte: 0.5 M H₂SO₄, 0.4 M HCl, 0.01 M FA and 0.5 mM HZ.

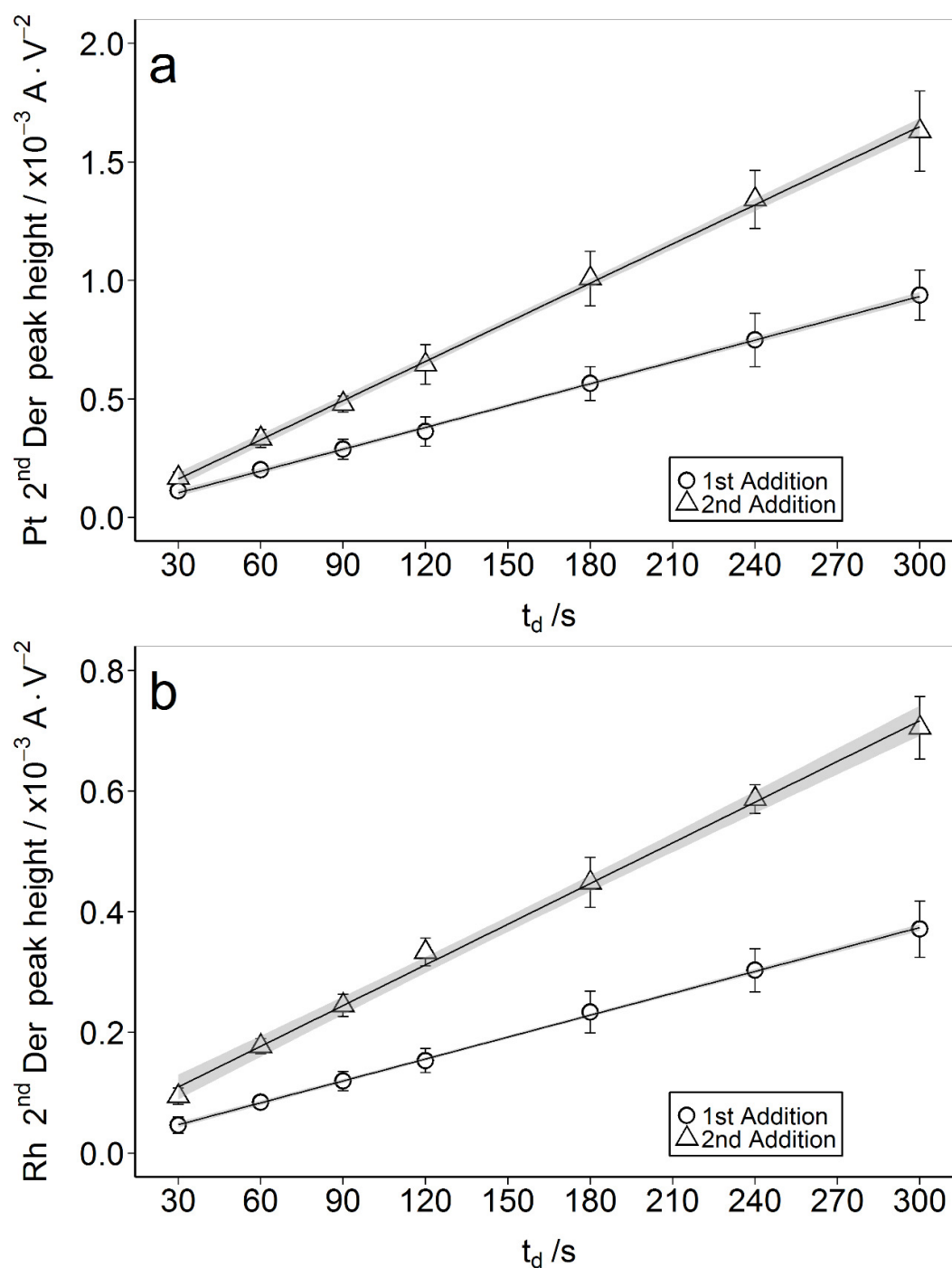


Figure 4 – Effect of deposition time, t_d , in second derivative (2nd Der) peak heights, measured using optimised conditions: **(a)** Pt: 2.0 ng L^{-1} , 2nd Der peak height = $1.2 \times 10^{-5} + 3.1 \times 10^{-6} t_d$ (circles) and 4.0 ng L^{-1} , 2nd Der peak height = $-1.7 \times 10^{-6} + 5.5 \times 10^{-6} t_d$ (triangles) and **(b)** Rh: 0.66 ng L^{-1} , 2nd Der peak height = $1.1 \times 10^{-5} + 1.2 \times 10^{-6} t_d$ (circles) and 1.3 ng L^{-1} Rh, 2nd Der peak height = $4.2 \times 10^{-5} + 2.2 \times 10^{-6} t_d$ (triangles). $E_d = -0.75$

V. Electrolyte: 0.25 M H_2SO_4 , 0.05 M HCl , 0.01 M FA and 0.5 mM HZ. The grey shaded area represents the 95 % confidence interval of the curve.

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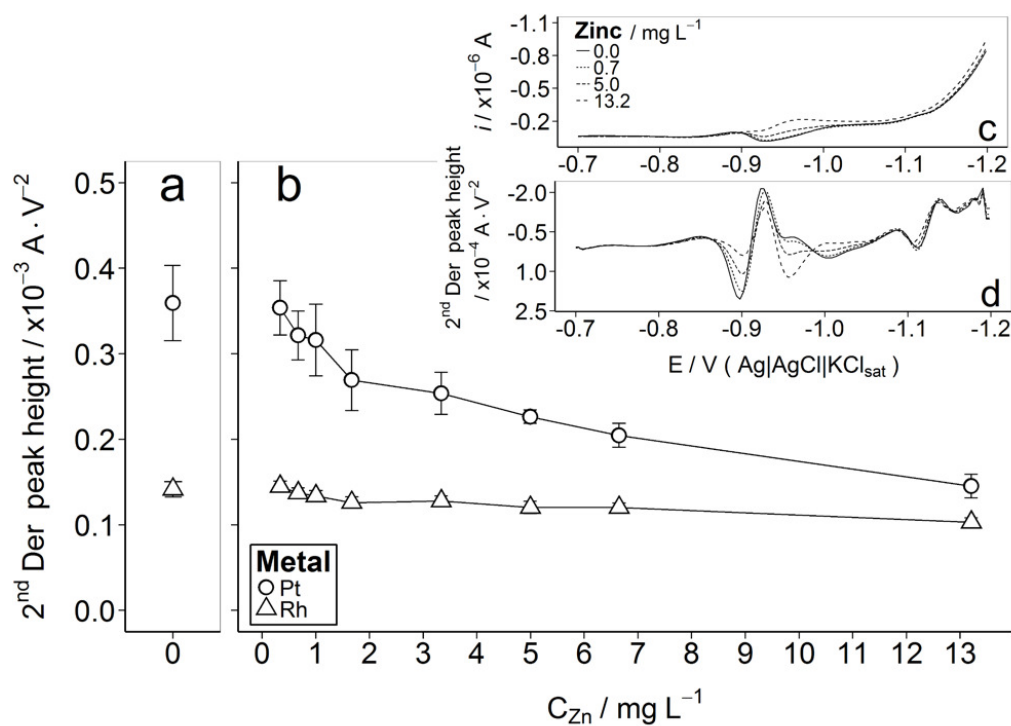


Figure 5 – Effect of Zn in peak heights of 1.0 ng L^{-1} Pt (circles) and 0.33 ng L^{-1} Rh (triangles) measured using the second derivative (2nd Der) transformation in optimised conditions: (a) without any Zn concentration (0 mg L^{-1}), and (b) Zn ranging up to 13 mg L^{-1} ; (c) original and (d) second derivative transformation voltammograms. $t_d = 120 \text{ s}$ and $E_d = -0.75 \text{ V}$. Electrolyte: $0.25 \text{ M H}_2\text{SO}_4$, 0.05 M HCl , 0.01 M FA and 0.5 mM HZ .

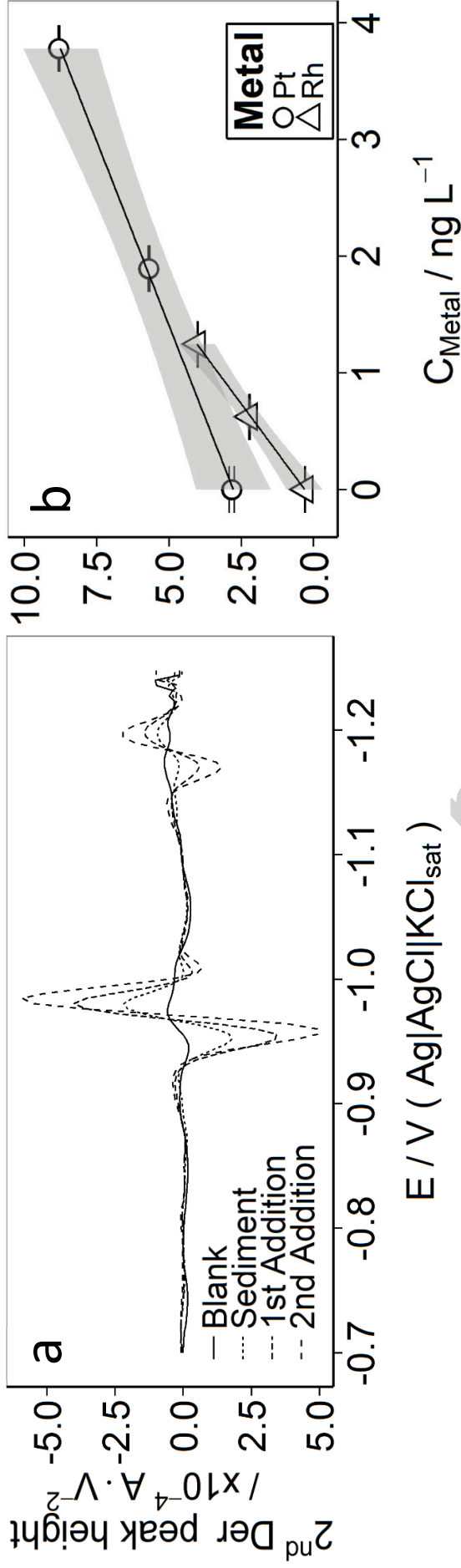


Figure 6 – (a) Second derivative (2nd Der) voltammograms of sediment sample #B, obtained in the optimised conditions: 1) blank (solid line); 2) sediment #B (500 μL of sample digest in 15 mL) corresponding to 1.6 ng L^{-1} Pt and 0.05 ng L^{-1} Rh (small dotted line); 3) first standard addition (dotted line), 1.9 ng L^{-1} Pt and 0.6 ng L^{-1} Rh; and 4) second standard addition (long dotted line), 3.8 ng L^{-1} Pt and 1.2 ng L^{-1} Rh. $t_d = 120 \text{ s}$ and $E_d = -0.75 \text{ V}$. Electrolyte: 0.25 M H_2SO_4 , 0.05 M HCl , 0.01 M FA and 0.5 mM HZ. (b) Calibration curve plot of 2nd Der peak heights ($n = 8$) with two standard additions, respectively: Pt (circles), 2nd Der peak height = $5.4 \times 10^{-5} + 6.0 \times 10^{-6} C_{Pt} \text{ ng L}^{-1}$, $r = 0.999$; and Rh (triangles), 2nd Der peak height = $3.2 \times 10^{-6} + 3.2 \times 10^{-6} C_{Rh} \text{ ng L}^{-1}$, $r = 0.999$. The grey shaded area represents the 95 % confidence interval of the curve.

Table 1 - Optimised experimental conditions used for both Pt and Rh determination in different matrices.

Electrolyte		
H ₂ SO ₄	0.25	M
HCl	0.05	M
FA	0.01	M
HZ	0.5	mM
Parameters		
Temperature	25 ± 2	° C
Equilibration and Purging time	10	min
Deposition potential	−0.75	V
Deposition time	120	s
Quiescent time	10	s
Initial potential	−0.7	V
End potential	−1.2	V
Scan rate	20	mV s ^{−1}
Modulation amplitude	25	mV
Modulation time	0.04	s
Interval time	0.2	s
Step potential	4	mV
Signal transformation	Smoothing SG 2 + 2 nd derivative	

Table 2 - Analytical characteristics of the method for the simultaneous determination of Pt and Rh: LOD, limits of detection, LOQ, limits of quantification, RSD, relative standard deviation; experimental conditions: electrolyte 0.25 M H₂SO₄, 0.05 M HCl, 0.01 M FA and 0.5 mM HZ; t_d =120 s and E_d = -0.75 V.

	Platinum			Rhodium		
	ng g ⁻¹ *	ng L ⁻¹	mol L ⁻¹	ng g ⁻¹ *	ng L ⁻¹	mol L ⁻¹
LOD	0.02	0.20	0.8 x 10 ⁻¹²	0.01	0.08	0.8 x 10 ⁻¹²
LOQ	0.06	0.50	3 x 10 ⁻¹²	0.03	0.20	2 x 10 ⁻¹²
Sensitivity (average slope) (A V ⁻² / mol L ⁻¹)			(2.9 ± 0.5) x 10 ⁷			(2.5 ± 0.6) x 10 ⁷
(A V ⁻² / ng L ⁻¹)			(1.5 ± 0.2) x 10 ⁻⁴			(2.4 ± 0.6) x 10 ⁻⁴
RSD						
(%)	17			20		

*Calculated for a digestion using 0.2 g of solid sample in 25 mL.

Table 3 - Determination of Pt and Rh (mean \pm SD) in road dust CRM BCR-723 and

environmental samples. Experimental conditions: electrolyte 0.25 M H₂SO₄, 0.05 M

HCl, 0.01 M FA and 0.5 mM HZ; $t_d=120$ s and $E_d = -0.75$ V.

Recoveries (%)		Platinum	Rhodium	Pt/Rh
CRM BCR-723	(n = 7)	87 \pm 12	90 \pm 10	6
Spiked Solution	(n = 5)	100 \pm 5	95 \pm 9	
Samples				
Tagus Estuary Sediments (ng g ⁻¹)	(n = 4)			
	#A	3.50 \pm 0.03	0.14 \pm 0.04	25
	#B	6.8 \pm 0.9	0.53 \pm 0.08	13
Urban WWTP Waters* (ng L ⁻¹)	(n = 4)			
Before the rain				
	Inflow	16 \pm 2	0.24 \pm 0.08	67
	Outflow	5.0 \pm 0.7	0.3 \pm 0.1	18
Soon after the rain				
	Inflow	25 \pm 2	0.17 \pm 0.06	147
	Outflow	10.0 \pm 0.3	0.19 \pm 0.02	53

* Dissolved fraction (< 0.2 μ m). Deposition time was increased for 300 s, LOD: Pt = 0.05 ng L⁻¹ and Rh = 0.04 ng L⁻¹

Highlights

- Dissolved Rh concentrations are reported for wastewaters for the first time.
- 2nd Der transformation improves the signal in simultaneous determination of Pt and Rh.
- LOD are adequate for ultra-trace Pt and Rh quantification in environmental matrices.
- Optimised method reduces time of analysis and reagents consumption.
- The method is suitable for routine analysis towards the knowledge of Pt and Rh cycle

