Improving the voltammetric quantification of ill-defined peaks using second derivative signal transformation: Example of the determination of platinum in water and sediments

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The determination of trace elements using stripping voltammetry may be seriously affected by the presence of intensive matrix background or interfering peaks, leading to poorer detection limits and/or inaccurate quantitative results. In this work we have tested the use of signal transformation (e.g. second derivative) in the analysis of platinum in seawater and sediment digests by means of catalytic adsorptive stripping voltammetry. In natural waters, the limit of detection of Pt is affected by a broad background wave due to the formazone complex used in the sample matrix for its determination, while in sediment digests, the Pt peak may be interfered by the presence of elevated concentrations of Zn affecting the accuracy of the determination. Results applying second derivative signal transformation revealed a significant improvement (2-3 fold) of the detection limit in water due to the minimization of background effects, therefore allowing shorter accumulation times and faster determinations. In the presence of interfering peaks, the inaccuracy resulting from erroneous baseline selection in the original signal is eliminated when the second derivative is used. Signal processing should be considered as a useful tool for other voltammetric methodologies where more accurate or faster determinations are needed.
Introduction

Platinum (Pt) cycle at the Earth’s surface is greatly impacted by anthropogenic activities, amounting up to – at least – 80% of its total mobilization. Among these activities, the use of Pt in automotive catalytic converters – which accounts for about 45% (average 2003-2012; http://www.platinum.matthey.com/publications/market-data-tables) of the total World demand – has not only been identified as the major source of Pt contamination in areas close to vehicular traffic, but has also served as evidence for a global Pt environmental disturbance.

A major challenge in any environmental study of Pt is the need for extremely sensitive analytical techniques that allow measuring its ultra-trace concentrations of $10^{-2}$-$10^{-1}$ ng g$^{-1}$ in sediments and $10^{-2}$-$10^{-2}$ pM in waters. Two analytical techniques, inductively-coupled plasma mass spectrometry (ICP-MS) and voltammetry, have been mostly used for the determination of Pt in water and sediments since they provide the sensitivity needed. The use of ICP-MS offers the advantage of a direct and rapid analysis of sediment digests and freshwater, provided the isobaric interference of $^{179}$Hf$^{16}$O on $^{195}$Pt, the commonly monitored Pt isotope, is taken into account. ICP-MS has also been used for the analysis of Pt in seawater where an anion exchange resin is used for the removal of sea-salts and preconcentration of Pt, and high-purity concentrated acids are used in the elution step making the procedure expensive, contamination-sensitive, time-consuming and thus unsuitable for routine analysis. The analysis of natural waters using voltammetry, however, appears to be more straightforward since no prior preconcentration step or removal of salts is required and is capable of determining Pt down to about 30 fM in seawater.

A potential drawback in voltammetric determinations arises when the target signal is affected by an intense background or interfering peaks that can strongly affect the
accuracy of the analytical quantification \(^{12,13}\). For example, the analytical peak in the voltammetric determination of Pt is obscured by a broad background wave, therefore requiring accumulation times as long as 15-30 minutes to obtain a discernible analytical peak at sub-picomolar concentrations. This implies that an analytical determination of an aliquot using the method of standard addition may last for several hours. In such scenarios where there exists signal overlapping or interferences, the application of derivative techniques has been proved to be useful for analytical purposes \(^{14-16}\). The use of derivative signal – generally the second derivative – has been commonly applied in spectrophotometric techniques where the target peak is obscured by an intensive background or interfering peak \(^{15,17}\). Despite the evident advantages that derivative techniques may offer in such cases, their applications to voltammetric analysis has been uncommon.

Here we demonstrate that second derivative signals can be used to overcome voltammetric procedures affected by the presence of broad background or interfering peaks, allowing shortening the accumulation times and increasing the accuracy of the determinations.

**Experimental Section**

*Material and Chemicals.*

All laboratory work was performed in a laminar flow bench (ISO-5) housed inside an ISO-7 lab. Voltammetric experiments were carried out using a \(\mu\)Autolab Type III potentiostat (Metrohm Autolab B.V.) connected to a polarographic stand (Metrohm model 663VA) equipped with a hanging mercury drop electrode (HMDE, working electrode), a Ag/AgCl (reference electrode), and a glassy carbon rod (counter electrode).
A polytetrafluoroethylene (PTFE) voltammetric cell was used in all experiments. Solutions in the voltammetric cell were stirred using a rotating PTFE rod, and the highest rotation speed (3000 rpm) was selected. Mercury used was for analysis and polarography (EMSURE®, Merck); the largest drop size (0.52 mm²) was selected. The potentiostat was controlled using the GPES v. 4.9 software (EcoChemie B.V.). Sulfuric acid (≥95%; TraceSELECT®, Fluka), formaldehyde (36.5%, Riedel-de-Haën), and hydrazine sulfate (p.a., Fluka) were used. Solutions of 1.46% (w/v) formaldehyde and 50 mM hydrazine were prepared in Milli-Q water and stored in 30 mL fluorinated ethylene propylene (PFE) bottles (Nalgene); these solutions were stable for several weeks. The breakdown of organic matter in the water samples, necessary for the determination of total dissolved Pt, were achieved by means of UV oxidation; samples were placed in capped quartz tubes and irradiated for two hours using a 125-W high-pressure mercury lamp as described earlier. The mercury lamp was placed in a fume hood located inside the ISO-7 lab. For sediments, samples were ashed in quartz crucibles, acid-digested using 30 mL screw-capped perfluoroalkoxy (PFA) vials (Savillex) and a time-temperature controlled Teflon-coated hot plate (SFH 5013 HD & TR 1040 PicoTrace GmbH). High-purity nitric (65%) and hydrochloric (30%) acids were employed (Suprapur®, Merck).

Procedure for the Determination of Pt in Water.

An aliquot (10 mL) of UV-digested sample was pipetted into a PTFE voltammetric cell. Aliquots of H₂SO₄ (300 µL of 17.7 M), formaldehyde (65 µL of 1.46%) and hydrazine sulfate (95 µL of 50 mM) were added directly to the sample. The final concentrations of the reagents in the sample solution were as follows: 0.5 M H₂SO₄, 3.3 mM formaldehyde, and 0.45 mM hydrazine. The sample solution was then deaerated by
purging with humidified N₂ (99.999%; Alphagaz™ 1, Air Liquide) for 5 minutes prior to analysis. A new mercury drop was extruded and the potential was set at -0.3 V for the desired accumulation time, while the solution was stirred at 3000 rpm with the PTFE rod. Then, stirring was stopped and, after a quiescent period of 10 s, a stripping scan was performed from -0.5 V to -1.1 V in the differential pulse (DP) mode at a scan rate of 20 mV/s using a modulation time of 0.04 s, an interval time of 0.2 s, a modulation amplitude of 25 mV, and a step potential of 4 mV. Platinum concentration in the cell was determined using the method of standard additions (Figure S1).

Procedure for the Determination of Pt in Sediments.

Prior to the acid digestion, sediments were ashed at 800°C for 3 hours, following the heating scheme given by Nygren et al. 18, in order to remove refractory organics that may interfere during the voltammetric determination 18. Ashed sediments were digested using a mixture of 5 mL conc. HCl and 3 mL conc. HNO₃ at 195°C for 4 hours. Then, samples were allowed to cool down, caps were removed and the acid was evaporated until near dryness. The residue was then redissolved adding 1 mL of conc. HCl and 1 mL of H₂SO₄, and evaporated again until no fumes were observed (i.e. only H₂SO₄ was present). This was diluted with 0.1 M HCl and syringe-filtered using a PFA syringe (Savillex) and 25 mm polyethersulfone membranes with 0.45 μm pore size (VWR), and then stored in 25mL polypropylene volumetric flasks (Nalgene). The voltammetric determination of Pt in the diluted digests was then carried out using the same procedure for waters, except that the UV irradiation was not necessary.

Procedure for Data Treatment.
Routines/algorithms included in GPES 4.9. software were used for all data treatments. Before applying any derivative transformation, original voltammogram is smoothed according to the Savitsky-Golay algorithm. For the signal-to-noise ratio in our voltammograms, a smoothing factor of 2 gave satisfactory results. Note that smoothing procedure is an important step in performing derivative transformations since the existing noise (in any transformation) could overpass signals in subsequently derived data. Derivative transformation of smoothed data was accomplished by using the following equation:

\[
\frac{dy}{dx}(n) = 0.5 \left( \frac{y(n) - y(n - 1)}{x(n) - x(n - 1)} \right) + 0.5 \left( \frac{y(n + 1) - y(n)}{x(n + 1) - x(n)} \right)
\]

where \(y\) and \(x\) are the current (in A) and potential (in V), respectively, and \(n\) indicates each of the data points.

The increase in the order of the derivative enhances the scan resolution and the detectability of minor signals/peaks, but results in worse signal-to-noise ratios (SNR)\(^\text{15}\). We have opted to use the second derivative signal as it is more efficient in eliminating the background interferences than the first derivative \(^\text{17}\), while keeping good peak-shaped transformed signals and better SNR than higher derivative orders. Second derivative data were obtained by applying twice the derivative transformation (double derivation). Note that after first derivation, data were smoothed again in order to eliminate noise accumulation.

**Samples**

The estuarine water was collected from the shore in the Vigo Ria (NW Iberian Peninsula; Salinity ~32) using a telescopic arm, filtered through a 0.2 µm polyethersulfone membrane (Millipore) and acidified to pH 1 with conc. HCl (Fluka
TraceSelect). The SAFe samples (S1 denotes surface and D1 and D2 denote 1000 m) were collected aboard the RV Melville in October 2004 at the SAFe station in the eastern North Pacific Ocean. The GEOTRACES intercalibration samples were collected in the Sargasso Sea aboard the RV Knorr at a station in the western North Atlantic Ocean in June 2008 and consist of a surface (GS) and 2000 m (GD) water for dissolved trace-metal intercomparison studies. Further details on these reference materials can be found at http://www.geotraces.org/science/intercalibration. The sediment sample used in this work corresponds to the river sediment certified reference material JSd-2 (Geological Survey of Japan).

Results and Discussion

In formaldehyde-hydrazine-sulfuric acid medium, a very sensitive hydrogen reduction current of catalytic nature is produced in the presence of small amounts of Pt (II and IV)\(^1\)\(^{11,19}\). The mechanism involves the formation of a complex of formazone – resulting from the reaction of formaldehyde with hydrazine – with Pt(II) (any Pt(IV) is reduced quantitatively to Pt(II) by hydrazine) which is adsorbed at the surface of the mercury electrode \(^1\)\(^9\) (see mechanism in Figure S2). It was suggested that the Pt(II)/Pt(0) reduction potential coincides with the observed catalytic hydrogen reduction current and that active centers of metallic Pt formed at the electrode surface decreases the hydrogen reduction overpotential; this mechanism would explain the drop in hydrogen production – causing the peaked shape of the current-potential plot – when the potential becomes more cathodic than the peak potential during a potential scan in the negative direction\(^1\)\(^1\)\(^{11,19}\) (Figure 1a).
Taking advantage of this sensitive catalytic hydrogen reduction current, adsorptive cathodic stripping voltammetric procedures have been developed and applied for the ultra-trace determination of Pt element in a variety of matrices\(^2,11,20\). Since the hydrogen reduction peak depends on the amount of Pt(II)-formazone complex adsorbed on the electrode surface, the analytical sensitivity increases at higher accumulation times. For example, a detection limit as low as 20-30 fM has been estimated in natural waters using accumulation times of 20-30 min\(^7,11\). This catalytic hydrogen analytical signal appears, however, superimposed on a broad wave due to the formazone complex; this makes the need of using long accumulation times at the low sub-picomolar Pt concentrations to obtain a defined peak to be used for its analytical determination (Figure 1a).

The improvement in the peak detection and quantification applying the 2\textsuperscript{nd} derivative signal is shown in Figure 1b. Here, a well-defined peak for Pt is obtained at low accumulation times (180 s) instead of the shoulder over the formazone wave observed in the original signal (Figure 1a). In order to examine whether the original and derivative signals provide the same concentrations, different aliquots of a UV-digested estuarine sample from the Vigo Ria (NW Iberian Peninsula) were analyzed by the method of standard additions at different accumulation times, expressed as sensitivity in order to correct for instrumental drift between determinations (Figure 2). The measure of the analytical signal in the derivative voltammograms were done using the peak-peak baseline\(^15,17\) whereas linear tangential baseline was applied to the original signal (Figure 1). The use of the original signal at low accumulation times, i.e. quantification based on an ill-defined peak, results in systematic lower concentrations than at high accumulation periods. This situation is overcome when the 2\textsuperscript{nd} signal derivative is used; here, the concentration obtained is not affected by the accumulation time used, being
identical to that obtained with the original signal at high accumulation periods, demonstrating the ability for quantitative determinations using this signal processing and the advantage of using shorter accumulation times thus decreasing significantly the time required for analysis.

Inaccuracy in the quantitative determination of a target analyte in the presence of an interfering peak is exemplified in Figure 3a. Here, the determination of Pt in sediment digests may be complicated by the presence of Zn, which, despite its lower sensitivity under the analytical conditions, is present at concentrations several orders of magnitude higher than Pt. Depending on the baseline used to calculate the peak height in the original signal (Figure 3a) – single-peak linear baseline (b1), double-peak linear baseline (b2) or linear front baseline (b3), which normally relies on the operator experience and/or subjectivity – significantly different concentrations are obtained (Table 1) that may lead to inaccurate results. This situation is overcome using the second derivative (Figure 3b), where there is no ambiguous determination of the peak current using the peak-peak baseline and provides accurate determination of the concentrations (Table 1).

**Blanks and detection limits in water**

The value of the blank (MQ water + reagents) using 2nd derivative with the peak-peak baseline resulted in a blank of $76 \pm 6 fM$ ($n=9; \text{using 300 s accumulation time}$), leading to a detection limit for Pt in water in this study, i.e. $\sim 20 fM$ (3xSD of the blank), which is similar or slightly lower than those previously reported using the original voltammetric signal but at higher accumulation times (10-30 min $^7,11$), proving the ability of the second derivative signal to reduce the analysis time in voltammetric analysis.
Currently, there are no certified reference materials (CRMs) for Pt in waters. The only water CRM for which Pt values have been given by different research groups is SLRS-4 (river water; NRC, Canada). However, the reported concentrations are not consistent: 6.7 ± 0.5 pM \(^{21}\), <0.15 pM \(^{22}\), and 7.6 ± 0.6 pM \(^{6}\) (Figure 4). Using the method described in this study, we obtained a concentration of 0.97 ± 0.09 pM (\(n=2\)). The unsuitability of these CRMs for Pt was also confirmed by the analysis of CASS-4 (nearshore seawater; NRC, Canada) and NASS-5 (ocean water; NRC, Canada); here, for example, analysis of aliquots of three different bottles of CASS-4 resulted in values ranging from about 7 to 15 pM. Also, these values clearly exceed those typical for marine waters \(^{7}\) indicating a random Pt contamination in these CRMs.

In order to provide Pt concentrations in certified reference water samples collected, handled, and processed using trace-metal clean techniques, SAFe and GEOTRACES intercalibration samples were analyzed (see Sample collection). Information on how to obtain these samples can be found on the GEOTRACES website (www.geotraces.org). In general, data from the GEOTRACES samples show a reasonable agreement (see Table 2), with differences between bottles of around 20% at the sub-picomolar level at which Pt is present. It is interesting to note that the average value for the GEOTRACES deep sample (211 ± 25 fM) agrees with the data of Colodner \(^{23}\) who also reported water profile Pt data at the same station about three decades ago – constituting the only Pt data in the Atlantic Ocean to date – and provided an average Pt of 260 ± 80 fM. There are also consistent lower surface concentrations at surface compared to deeper waters, being especially evident for the Pacific samples (SAFe). The increase of Pt concentrations with depth in the Pacific Ocean was also observed by Goldberg et al. \(^{24}\), although the values found in this study are about 5 times lower than those previously reported by
Goldberg et al. 24, evidencing our current gaps in our knowledge of Pt concentrations and behavior in the marine environment.

Conclusion

In this study, it has been demonstrated that the use of signal processing in stripping voltammetry is an effective mean for increasing the scan resolution and minimizing baseline effects and matrix interferences, enabling an accurate determination reducing the time required for analysis. The improved analytical capabilities that signal processing may offer in environmental studies are especially critical for elements like Pt which are subject to a significant current disturbance of their cycle at the Earth’s surface due to human activities, but whose biogeochemical behavior in the environment is not yet well constrained due in part to the highly time-consuming analytical techniques available so far for its determination at ultra-trace levels.

Acknowledgement

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Supporting Information
Additional information is available as described in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

References


Figure 1. Original and 2nd derivative voltammetric scans obtained in a sample from the Vigo Ria at 180s and 600s accumulation time. Conditions: 0.5 M H₂SO₄, 3.3 mM formaldehyde, 0.45 mM hydrazine. Platinum concentration in cell ~ 0.55pM, obtained from the method of standard additions using the original signal at an accumulation time of 600s. The linear baseline (original signal) and peak-peak baseline (2nd derivative) used for the calculation of the signal are shown for the scans measured using 180s accumulation time.
Figure 2. Concentrations obtained in a sample from the Vigo Ria at different accumulation times (expressed as the sensitivity). The dependence of the sensitivity on the accumulation times (from 3 to 10 min) was $2.7 \pm 0.4$ nA/pM-min and $1.2 \pm 0.2$ nA/V$^2$·pM-min for the original signal and the 2nd derivative, respectively. The solid and dashed lines represent the average value and the 2xSD, respectively, of the concentrations obtained using the 2nd derivative.
Figure 3. Voltammetric scans of a diluted digested sample of a river sediment certified reference material (JSd-2). Conditions: 0.1M H$_2$SO$_4$, 3.3mM formaldehyde, 0.45mM hydrazine. (a) Original signal; (b) second derivative. Platinum concentration in cell ~ 20pM
Figure 4. Comparison of reported data of Pt on various reference materials for natural waters with the values obtained in this study. The three different values given for CASS-4 in this study correspond to three different bottles.
Table 1. Platinum concentrations obtained for the river sediment certified reference material JSd-2 using the original signal and the second derivative ($n$=3).

<table>
<thead>
<tr>
<th></th>
<th>Pt (ng g$^{-1}$)</th>
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<tbody>
<tr>
<td>Original Signal</td>
<td></td>
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<tr>
<td>Baseline b1</td>
<td>6.2 ± 1.0</td>
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<tr>
<td>Baseline b2</td>
<td>8.1 ± 1.0</td>
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<tr>
<td>Baseline b3</td>
<td>14.5 ± 2.5</td>
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<tr>
<td>Second Derivative</td>
<td>Peak-peak baseline</td>
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<tr>
<td>Certified Concentration*</td>
<td>16.7 ± 2.8</td>
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*Average of the indicative value given by the Geological Survey of Japan and those reported in the literature$^2$

Table 2. Results for Pt determination in GEOTRACES and SAFe intercalibration samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bottle Number</th>
<th>Pt (fM)</th>
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<tbody>
<tr>
<td>GEOTRACES Intercalibration</td>
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<tr>
<td>GS</td>
<td>179</td>
<td>142 ± 8 ($n$=3)</td>
</tr>
<tr>
<td></td>
<td>008</td>
<td>173 ± 8 ($n$=2)</td>
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<tr>
<td>Mean GS</td>
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<td>154 ± 18 ($n$=5)</td>
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<tr>
<td>GD</td>
<td>196</td>
<td>194 ± 11 ($n$=3)</td>
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<tr>
<td></td>
<td>085</td>
<td>237 ± 11 ($n$=2)</td>
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<tr>
<td>Mean GD</td>
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<td>211 ± 25 ($n$=5)</td>
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<td>SAFe Intercalibration</td>
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<tr>
<td>S1</td>
<td>070</td>
<td>83 ± 5 ($n$=5)</td>
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<tr>
<td>D1</td>
<td>181</td>
<td>196 ± 4 ($n$=3)</td>
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<tr>
<td>D2</td>
<td>327</td>
<td>227 ± 51 ($n$=5)</td>
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Ill-defined Pt peak

Second-Derivative Signal Transformation