



## Unusual PLS application for Pd(II) sensing from extreme acidic solutions

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A very cheap and extremely selective device, TazoC-Mar@, for Pd(II) determination from very acidic solution is presented. The sensor is prepared *via* ion exchange of an azoic ligand, (2-(tetrazolylazo)-1,8 dihydroxy naphthalene-3,6,-disulphonic acid), named TazoC, on the Macroporous Strong Anion Exchange Resin, Marathon<sup>®</sup> (Dow Chemical-USA). The TazoCMar@ reacts very quickly with palladium(II) solutions through formation of a complex that gives, even at formal pH=0, an intense blue colour to the solid phase. At this pH no other metal ion, not any precious metal ions, not any ubiquitous metal ions such as Al(III) and Mn(II), even if present at much high concentration, reacts with the device, making TazoC-Mar@ extremely selective for Pd(II) sensing. Quantification is also possible. The analytical signal used for detection is the whole vis spectra of the coloured solid phase, (which apparently is of very poor quality) and applying the PLS, the partial least square regression, to relate the signals with the standard Pd(II) concentrations. The regression model obtained gives a good fitting and correct predictions of Pd(II) concentrations in unknown samples. For the validation the certified material "Road dust, trace elements, BCR 723" was employed. The operational values of LOD and LOQ are equal to  $2 \cdot 10^{-7}$ M and  $5 \cdot 10^{-7}$ M, respectively. Further improvement can be achieved.

### 1. Introduction

In the last decades, palladium has attracted a lot of attention in various fields, from industry to medicine, due to its excellent chemical and physical properties, including the noble metal character, alloying ability and catalytic activity. In particular, the increasing number of cars equipped with catalytic converters, made to reduce emission of gaseous pollutant in vehicles, has introduced into the environment novel anthropogenic metals including palladium, platinum and rhodium.<sup>1</sup> As consequence, the levels of these elements have increased in soils, plants, roads sediments and airborne particles. Environmental and health risks related to these new emerging pollutants have arisen. As consequence, on one hand the need related to the increasing area of palladium applications, on the other the need to assess this new contaminant have stimulated the development of analytical methods for palladium quantification.<sup>1</sup>

Instrumental methods such as electrothermal atomic absorption,<sup>2</sup> inductively coupled plasma atomic emission spectroscopy,<sup>3-5</sup> high performance liquid chromatography,<sup>6</sup> cathodic strip voltammetry<sup>7</sup> have been applied. In any case, even if most of these techniques exhibits a quick final

detection with high sensitivity, expensive instrumentation and complicated sample preparation are needed, often including a separation/preconcentration step prior to detection.<sup>2-3</sup>

Conversely, recent years have seen a great development of colorimetric probes that, if compared to common analytical techniques, offer the advantage to use simple and low cost instrumentation and feasibility to develop tailored sensors.<sup>8-10</sup> Based on that, we present here a cheap sensitive optical sensor for palladium detection and quantification, based on TazoC (2-(tetrazolylazo)-1,8 dihydroxy naphthalene-3,6,-disulphonic acid)<sup>11</sup> impregnated on a commercial Macroporous Strong Anion Exchange Resin, Marathon<sup>®</sup> (Dow Chemical-USA). The sulphonated azo-dyes are a family of ligands widely used as spectrophotometric reagents. We successfully blocked one of this on an anionic resin, and due its extreme sensitivity towards palladium,<sup>12</sup> we succeeded to perform analysis through solid-phase spectrophotometry in extreme conditions such as 1 M HNO<sub>3</sub>. For the final quantification, we took advantage from partial least square regression, PLS, a well know chemometric tool<sup>13-14</sup> of which we propose here an uncommon application.

For the validation of the method, the reference material, BCR 723, containing a multitude of other metal ions, was employed

### 2. Experimental

#### 2.1 Chemicals

All reagents were of analytical-reagent grade, milliQ water was used throughout.

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Palladium standard solutions were obtained by dilution of 1000 mg/L Palladium Standard for ICP CAS 7647-01-0 by Sigma Aldrich.

Sodium acetate (Sigma Aldrich CAS 127-09-3) was used to make a buffer sodium acetate/acetic acid at pH 4.5, ultrapure HNO<sub>3</sub> 65% (Fluka CAS 7697-37-2) to prepare solutions, 0.1M and 1M to have a formal pH equal to 1 and 0 respectively.

TazoC was synthesized, purified and characterized according to the previously described procedures.<sup>11</sup> Elemental analysis performed on the final product confirmed the empirical formula C<sub>11</sub>H<sub>5</sub>O<sub>8</sub>N<sub>6</sub>S<sub>2</sub> Na<sub>3</sub>·3H<sub>2</sub>O and MW equal to 536.34.

The anion exchange resin, Dowex Marathon in chloride form, 24-28 mesh, CAS Number 60177-39-1, was delivered by Sigma Aldrich. It was used after washing with 0.1 sodium hydroxide, then with HNO<sub>3</sub> 0.1M and finally several times with milliQ water. It was dried at the air and kept on a desiccator to be used when needed. In this form, it still contains some water. Drying a known portion in the oven at 80°C at constant weight, the dry resin is 87.0 %. The weighted amount is always referred in the following to the amount of dry resin.

The positive charge exchanging groups were determined by exchange of nitrate with perchlorate ions, according to usual method and found equal to 1.8 mmol/g of dry resin, in agreement with the declared content. In ESI<sup>†</sup>, figure S1, the SEM images of the resin, showing the typical styrenic structure of the skeleton, are reported.

### 2.2 Sorption kinetic and sorption profile of the TazoC on the Marathon.

Kinetic profiles and sorption isotherms were performed from different solutions with a discontinuous procedure. A series of 10 independent samples, with 20 mL of ligand at a known concentration, always equal to 1.25 10<sup>-3</sup>M in the case of the kinetic profile experiments, ranging from 0 to 3 10<sup>-2</sup>M in the case of sorption isotherms, were put in contact with 0.5 g of dry resin and left gently stirring on a shaking plate. At a given time for kinetic experiments, and after equilibration for sorption experiments, the agitation was interrupted, a sample of the water phase was drawn back and analysed for the ligand content, by Uv-vis spectrophotometry. The amount of sorbed ligand,  $q_{\text{TazoC}}$  (mmol/g), is determined by difference from the total content.

### 2.3 Preparation of the TazoC-Mar@

The immobilization of the ligand was *via* ion exchange. This strategy is similar to that described elsewhere for this family of ligands.<sup>15</sup> The amount of active sites was left in excess of at least 90% compared to the mmol of TazoC. In this way the possible competition of other anions, critical in a case of real samples, is minimized. In the present research, we prepared the solid sensor, referred in the following as TazoC-Mar@, contacting a ligand solution with a known amount of dry resin under the condition that the mmol of ligand were 5% of total mmol of active sites (TazoC has two negative charges). Typically, 20 mL of a solution of TazoC 1.25 10<sup>-4</sup> M were put in contact with 0.5 g of dry resin, left under gentle stirring until the complete ligand sorption.

### 2.4 Sorption kinetic and isotherms of metal ions on TazoC-Mar@.

The same procedure described above for the ligand sorption studies was adopted for studying the kinetic profiles and sorption of the cations on the solid phase. The difference is that, instead of the resin, we used TazoC-Mar@ as solid phase, and, instead of measuring the ligand, we evaluated the metal in solution and/or in the solid phase. For simplicity, TazoC-Mar@ was prepared directly in 10 independent samples, before metal addition, contacting 0.5 g of resin with 20mL of 1.25 10<sup>-3</sup>M ligand solution in acetate buffer 0.01 M or HNO<sub>3</sub> 0.1 or 1.0 M, depending on the pH selected for the experiment.

Then, a known metal ion concentration was added, equal to 4 10<sup>-5</sup> M in the case of the kinetic experiments, ranging from 0 to 6 10<sup>-3</sup> M in the case of isotherms. In both cases, the samples were left gently stirring on a shaking plate. At a given time for kinetic experiments, or after equilibration for isotherms, the agitation was interrupted, a sample of the water phase was drawn and analysed for the metal content by ICP-OES method. For some experiments, the solid phase was directly analysed reading the vis spectra (see below) vs a blank prepared with 0.5 g of TazoC-Mar@ equilibrated in a solution of the same composition of samples but without the metal ion.

The amount of sorbed metal,  $q_M$ , mmol/g, was determined by difference from the total initial content.

### 2.5 Vis spectra and colorimetric analysis in the solid phase.

The vis spectra of TazoC-Mar@ after equilibration were recorded in a 0.5 cm cuvette, filling the cuvette with a suspension of the solid in the equilibrating solution by a Pasteur pipette.



**Figure 1** Cuvettes filled with suspended solid phase in HNO<sub>3</sub> solution. From left to right, Marathon resin, TazoC-Mar@, TazoC-Mar@ after contact with Pd(II) solution.

As an example, in Figure 1, cuvettes filled as described are shown, respectively from left to right, the simple resin, the TazoC-Mar@, and the TazoC-Mar@ complexed with Pd(II), being the equilibrating solution HNO<sub>3</sub> 1M..

All the solid spectra reported in this paper were obtained following the above described procedure and using as blank a cuvette filled with non-complexed TazoC-Mar@.

### 2.6 Actual sample.

The certificated material (Road dust, trace elements, BCR 723), employed for validation, was obtained by Sigma Aldrich. See ESI<sup>†</sup>, Table S1 for further details on its composition.

An exactly weighted portion of about 0.3 g was mineral digested with 5 mL of ultrapure HNO<sub>3</sub> and 2.5 mL of H<sub>2</sub>O<sub>2</sub> at 30% v/v in the MarsXpress microwave system, supplied by CEM (CEM s.r.l., Cologno al Serio, Italy) in a Teflon sealed vessel at 800 W, with heating program of a ramp of 25 min to 220°C (max pressure 800 PSI), followed by 25 min at 220°C.

The solution was then evaporated to few mL and the residual diluted at 25 mL with milliQ water. The total metal content was determined by ICP-OES analysis.

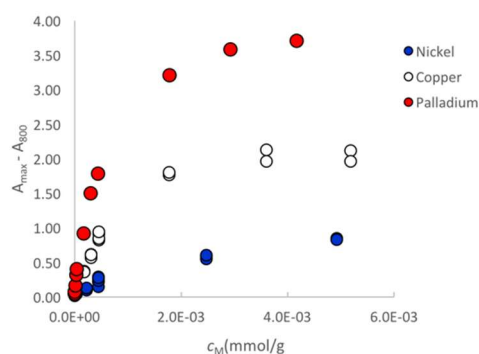
## 3. Results and discussion

In a preliminary screening, we evaluated different cations, in particular Cu(II), Ni(II) and Pd(II) as possible target analytes. Our first idea was to perform the analysis in a slight acid solution where not only the Pd(II) complex is formed, but also those of Cu(II) and Ni(II), hoping to obtain similar analytical response for different analytes and being in a position to apply PLS (we adopted the R-based chemometric software developed by the Group of Chemometrics of the Italian Chemical Society)<sup>16</sup> for determining the contribution to the vis spectra of each single analyte, as successfully done elsewhere.<sup>17</sup> The idea was to model the sorption spectra on the basis of a precise design of experiments<sup>18</sup> that guarantees the construction of an equilibrated non correlated matrix at the presence of these three metal ions. For this purpose, we performed spectra of TazoC-Mar@ equilibrated in solutions containing different mixtures of Pd(II), Cu(II) and Ni(II) at pH 4.5 (see ESI<sup>†</sup>, Table S2), but the validation step was successful only for Pd(II) and partially for Cu(II), (details can be found in ESI<sup>†</sup>, Figures from S3 a to S5 b). The unsatisfactory result is mostly caused by the response of TazoC-Mar@ towards Pd(II), ultimately too strong in term of the apparent molar absorptivity coefficient and stability of the complex. This can be seen in Figure 2, where the absorbance of the solid phase at maximum wavelength of the complex of three independent experiments for each metal ion is compared, as function of total metal concentration. These are definitively not the optimal conditions for a good PLS regression in the purpose of evaluating, in an unknown sample, the concentration of each analyte, when the response of each of them, in terms of sensitivity, is similar.

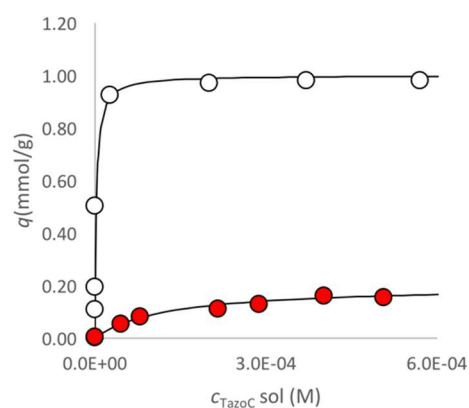
Furthermore, other problems arose when we supposed to carry out the external validation test, which is a fundamental step in PLS modelling. We found only very few reference materials for Pd(II), and we selected one of these product, the "Road Dust, trace elements, BCR 723" (see ESI<sup>†</sup> Table S1 for the declared composition) being the most suitable for our purposes. Unfortunately, in this sample Pd(II) is present at sub-trace levels, several order of magnitude lower than Cu(II), Al(III), Mn(II) and Fe(III), which are often 10<sup>6</sup> times more concentrated. All of these cations, at larger or lesser extension at pH = 4.5 are complexed by TazoC-Mar@, making Pd(II) determination impossible.

For all these reasons, we decided to move our strategy from a differential receptor towards a selective one, thanks to the strong affinity of Pd(II) for the active site that allows the formation of the complex between Pd(II) and TazoC at any pH even in 3M HClO<sub>4</sub>.<sup>12</sup> In such extremely acidic conditions other metal ions are not complexed, even if present at high concentration. For this reason, we explored the behaviour of TazoC-Mar@ device in ultra-acid region.

One of the main useful information when setting up an optical device is its maximum sorption capacity. This quantity can be obtained building sorption isotherms, as shown in Figure 3 for TazoC on the Marathon resin, at pH=0 and also at pH=4.5, i.e. the conditions chosen for the preliminary experiments.



**Figure 2** - Absorbance of the solid phase at the maximum wavelength of the complex at pH=4.5, V=20 mL, 0.5 g of TazoC-Mar@ after equilibration with increasing cation concentrations. Pd(II), red circles, Cu(II), white circles, Ni(II), blue circles.



**Figure 3** - Sorption profiles of TazoC on the Marathon resin. 0.5 g of resin, equilibrated with 20 mL of solution, at pH =4.5 (white circles) or, the pH =0 (HNO<sub>3</sub> 1M, red circles)

Comparing the two sorption profiles, it is evident the strongest retention of TazoC on the resin at pH=4.5. The fitting of the profile at this pH, according to Langmuir equation<sup>19</sup>, gives  $q_{\max}=0.976(5)$  mmol/g and  $K_L=4.0(2) \cdot 10^5 \text{ M}^{-1}$  (here and following, the figure in brackets is the uncertainty on the last digit).

The maximum sorption capacity, in such condition, referred to the mmol of TazoC (which exhibits two negative charges) to

the weight of the dry resin, is in pretty good agreement with 1.1 meq/mL declared for the resin as presented (according to Sigma Aldrich, the resin has a water content between 56-66%) and it is in perfect agreement with the value of 1.8 mmol/g found in the ion exchange experiment with perchlorate.

To minimize the interference of other anions that could be present in the water phase, and to avoid the colour saturation of the resin, once the ligand is sorbed, we decided to keep the quaternary positive group of the resin in large excess with respect to the mmol of TazoC, as done elsewhere, leaving at least 90% of active group in the nitrate form. Moreover, in this case, the solid phase TazoC-Mar@ presents an intense colour, avoiding too high absorbance values by performing measurement directly on the solid phase (see Figure 1). In our typical operational conditions, with 0.5 g of resin and solution volume of 20 mL, the optimal ligand concentration in solution was  $1.25 \cdot 10^{-3}$  M, obtaining a 0.05 mmol/g of TazoC sorbed on the resin (around 10% of active sites occupied). The relatively high amount of resin, 0.5 g, is needed just to easily fill the cuvette for spectrophotometric measurement. This low saturation of the resin active sites is also suitable for working in the acidic region. In such condition, as expected, the resin active sites are exchanged with nitrate and the apparent sorption capacity towards TazoC decreased dramatically, as shown in Figure 2, where the sorption profile in  $\text{HNO}_3$  1M, (formal pH= 0), is reported.. At this pH,  $q_{\max}=0.20(6)$  mmol/g (and  $K_L= 8.0(6) \cdot 10^3 \text{ M}^{-1}$ ), is lower but enough to have TazoC-Mar@ still stable without ligand leaching.

### 3.1 Kinetic study for TazoC-Mar@ preparation

The kinetic experiments were carried out to establish the suitable timing for TazoC-Mar@ preparation. In Figure 4, the kinetic sorption profiles of TazoC on Marathon from solutions at different pHs are reported. The stirring of the samples was kept constant on a vibrating plate.

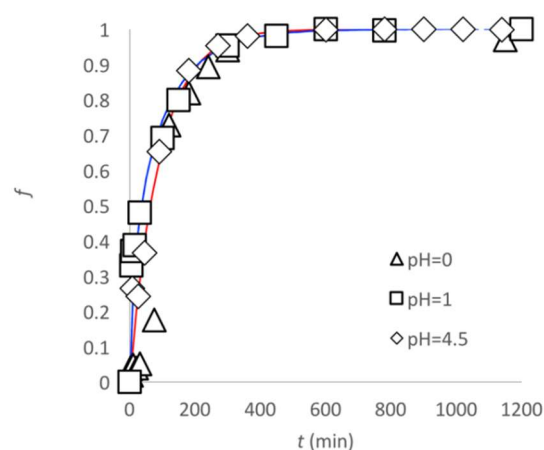


Figure 4 – Sorption kinetic profiles. 0.5 g of resin, equilibrated with 20 mL of TazoC  $1.25 \cdot 10^{-3}$  M solutions at different pH, as reported in the legend. The red lines are the fitting according to a film diffusion limiting process, the blue ones those obtained with a particle diffusion model<sup>19</sup>

As evident from the figure, there is no difference in the kinetic behaviour at pH 4.5, 1 and 0.

About the sorption model<sup>19</sup>, the profiles seem to be described better by a particle diffusion model, (see blue curve in Figure 4), instead of by the film diffusion model, (see red curve in Figure 4), but this is merely a qualitative indication. To assess the kinetic process which limits the sorption of TazoC on the resin, more experiments are needed and this lies outside the purposes to this paper.

We establish that usually 4 hours are more than enough for obtaining a complete sorption, and the TazoC-Mar@ ready for use.

### 3.2 Stability

To test reproducibility and stability of the device, 10 different TazoC-Mar@ portions of the same weight were left to equilibrate in 20 mL of buffer solutions at pH =4.5. From the vis spectra of the solid phase, the absorbance at  $\lambda_{\max}=610$  nm after 1 day and after 8 days was collected. Based on the result of the *t* test, the two mean values were not significantly different, at confidence level of 95%, meaning that the device is stable for at least one week. The reproducibility of each series was of 5 and 7%, respectively. The repeatability (calculated on the entire dataset of measurement, since neither standard deviations, neither mean values of each series were different) was 6%.

Since we lastly decided to use TazoC-Mar@ for Pd(II) sorption at pH=0, we tested the stability with 4 independent portions of TazoC-Mar@, measuring the absorbance 1, 4 and 7 days after preparation. The reproducibility for each series of measurement was again around 6%, so similar to that at pH 4.5. On the contrary, in this case the mean value of the absorbance over time decreases, and after 7 days was around 30% lower than after 1 day of contact. The ligand is not released, since the solution are not coloured, but plainly the ligand decomposed. So under this condition, the TazoC-Mar@ must be used just until 1 day after preparation. In this case the decreasing of the absorbance is within 5%.

### 3.3 Sorption kinetic of Pd(II) on TazoC-Mar@

Once the procedure for device preparation was established, the sorption of the Pd(II) into the solid was studied.

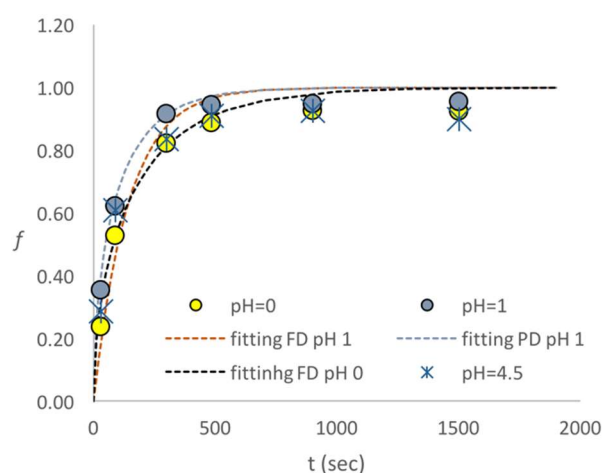


Figure 5 – Sorption kinetic profiles of Pd(II) under typical condition: around 0.5 g of TazoC-Mar@, in 20 mL of solutions at different pH and  $c_M$  around  $4 \times 10^{-5} M$ .

In figure 5, the sorption kinetic profiles of Pd(II) on TazoC-Mar@ under different pHs of the external solution are shown. There is almost any difference in the metal ion sorption and finally is always quantitative, in spite of the dramatic change in the external solution. The equilibration time is relatively fast, if compared to those usual for a biphasic equilibrium, and after 15 minutes is more than 90% of Pd(II) sorbed for all the three systems here examined.

### 3.4 Calibration curve at pH 0

Since the idea of performing the analysis at pH 4.5 failed because the problems previously described (see the first paragraph of page 3) we carried out the calibration of Pd(II) on TazoC-Mar@ at low pH.

In the first step, we collected the spectra as function of increasing amount of Pd(II) added in the solution phase, at pH=1 and 0, as shown in Figure 6 (here only spectra at pH =0 were reported). They are registered against a blank consisting of TazoC-Mar@ equilibrated in solution at the same pH, but without Pd(II). After equilibration, the absorbance of each sample was registered.

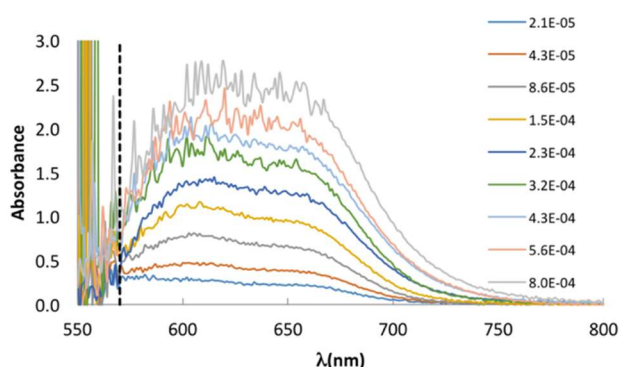


Figure 6 – Vis spectra of suspended TazoC-Mar@ in  $HNO_3$  1M, as function of increasing concentrations of Pd(II), as reported in captions where concentrations are referred to the solid phase (mmol/g), the blank being TazoC-Mar@ in  $HNO_3$  1M, without Pd(II).

The spectra result rather disturbed, especially at low wavelengths and at high Pd(II) concentrations. This is due to the limit of the technique itself, depending on the maximum A values that can be read by the instrument, and from the physical nature of the objects studied. Nevertheless, it is possible to perform a univariate analysis registering the absorbance at  $\lambda_{max}$  at 610 nm (subtracted to the absorbance at 800 nm, to prevent the effect of a possible drift, even if in this case it is not significant) vs. the Pd(II) concentrations referred

to the solid phase. It is possible to express the concentration in mmol/g of dry solid phase since no Pd(II) was left in solution after equilibration, at any concentration, as verified by ICP-OES analysis of the water phase. Data at pH=1 are omitted here and in the following since they look very similar to that at pH=0. They can be seen in ESI<sup>†</sup>, Figures S6, S7.

The dose/response curve obtained from spectra of Figure 6 applying univariate calibration, is shown in Figure 7.

The linear fitting gives a straight line, in a very restricted concentration interval, which becomes wider, at least of a magnitude order, if a second-order equation is used. It was not noticed any difference between the calibrations at the two different pH.

The parameters of the fitting are reported, for both the pH 0 and 1 in ESI<sup>†</sup>, table S3.

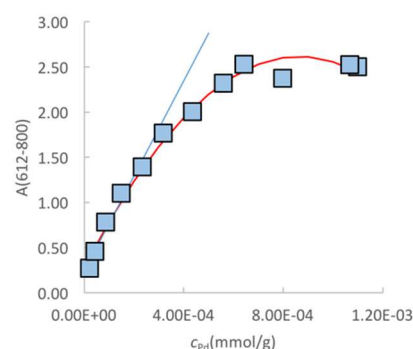


Figure 7 – The dose response curve using univariate data treatment, achieved from spectra reported in Figure 6. Net absorbance at  $\lambda=610$  nm is reported vs the concentration of Pd(II) in the solid phase. The straight line was obtained by linear regression on the first 6 points (blue line). The fitting reported in red was obtained performing polynomial regression (quadratic model) on all points.

Conversely, if the whole spectrum from 570 nm to 800 nm is used as x block of variables and the concentrations of Pd(II) as y block variable, only a multivariate regression such as the PLS model can be applied. Using this approach for each dataset related to each pH, two very different output are obtained, as summarized in graphs of Figure 8 (ma in Fig 8 è mostrato solo output per pH =0).

It is true that this is an unusual use of PLS, which was developed for having Y block as a matrix (id. different analytes, usually also many, in each column), conversely we have a vector, namely the column of Pd(II) concentrations. However, there is any real preclusion to use it, particularly here where a clear improvement is achieved remembering that we are dealing with an extremely poor quality of data, if compared with typical UV-vis spectra of solutions. The PLS analysis, without any other data treatment, which is often used in case of disturbed signals (for instance smoothing of data, baseline correction, etc. etc.), allows to empathized differences of the whole spectra, much more than differences within the spectra (noise).



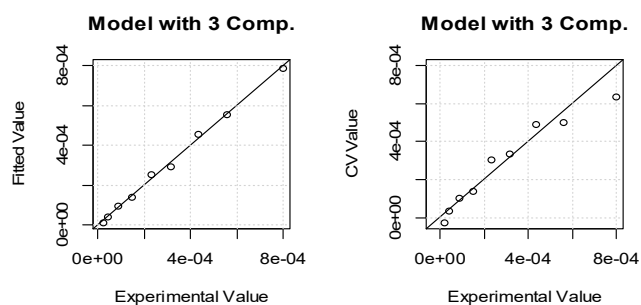


Figure 8— The results of the PLS for the system TazoC-Mar@/Pd(II) at pH=0 (spectra of Figure 6), on three latent variables. On the left the predicted values are reported against the known Pd(II) concentrations (mmol/g); on the right, the same in cross validation.

### 3.4 Model validation, LOD and LOQ

The fitting ability is an important feature of a model, but for an analytical application, it is much more important the ability to correctly predict the concentration in unknown samples. For testing this property, a series of independent samples of known concentration are analysed as if they were unknown: in PLS analysis they are called test set.

The results of the predicted vs the true values are shown for the univariate and multivariate models in figures 9a and 9b.

In the both figures, results obtained on the test set are reported with empty circles. In the same graphs, with asterisks, the results obtained analysing the reference material enriched with different Pd(II) concentrations are also reported.

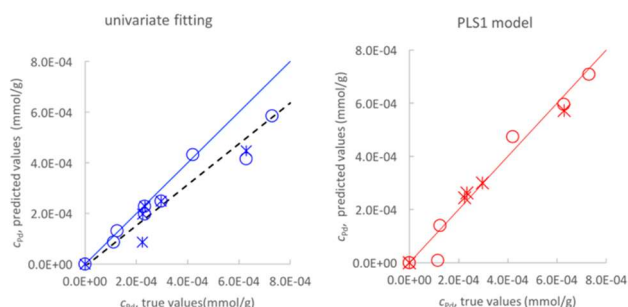


Figure 9 – The predicted values vs. the true ones in the case of univariate data treatment (quadratic equation) on the left, and in the case of PLS model on the right, both referred to data at pH=0.

External data set is reported with circles, enriched reference material with asterisk.

For the first samples, we prepared an independent test set, and at this stage, was not included in the model. In the case of reference material, Pd(II) was added prior the microwave digestion and the true values are those determined by ICP-OS measurements.

It is worth to note that the reference material without Pd(II) addition did not significantly coloured the TazoC-Mar@, meaning that at pH=0 no other metal, even if present at high concentration, is able to be complexed by the solid.

The values predicted by the univariate regression, through the second-order equation, are reported vs. the true values, in the blue graph of Figure 9a, while the results obtained by PLS are reported in the red graph of Figure 9b.

In principle, if a model is able to predict correctly the true concentration, a straight line with slope equal to one and intercept equal to zero is expected (see continuous line in the graphs). Here the predictive ability of the PLS model is evident. Only in the case of multivariate regression a straight line such that expected is found (at confidence level of 95%), while in the case of univariate regression a straight line with slope significantly different from one is obtained (always at  $v=0.95$ ); it is reported in the blue graph of Figure 9a as a dotted black line.

We also performed the LOD determination. For this purpose, the spectra of 9 different portions of TazoC-Mar@ equilibrated in solution at pH =0 and  $c_{Pd} 2 \cdot 10^{-5}$  mmol/g were registered. This Pd(II) concentration is chosen since it is supposedly close to a quantification limit. The spectra were submitted to the PLS model and the Pd(II) concentrations predicted. The mean value was found equal to  $1.8(6) \cdot 10^{-5}$  mmol/g.

We included this data set into the model and we predicted the concentration of Pd(II) in 10 new samples of blank, i.e. TazoC-Mar@ equilibrated in  $HNO_3$  1 M, without Pd(II). We used 3 times the standard deviation of this data set to establish a LOD value and 10 time to establish a LOQ values and they were found to be  $6 \cdot 10^{-6}$  mmol/g and  $2.1 \cdot 10^{-5}$  mmol/g, respectively. They correspond, working under our usual conditions, namely 0.5 g of solid phase in 20mL of solution, to operational values of LOD and LOQ equal to  $2 \cdot 10^{-7}$  M and  $10^{-7}$  M. Of course, increasing the preconcentration ratio and working for instance with a volume of 200mL, they become 10 times smaller. It is surprising that with such poor data and materials we reach such level of performance.

As final comment, we ultimately focused on performing analysis at formal pH=0. The quality of the signal was very similar between 0.1 M and 1 M  $HNO_3$ , and consequently also those of modelling. As long as Pd(II) complexation is concerned, there is no difference operating at the two  $HNO_3$  concentrations, but this could be not the case when other metal ions are present in the solution. Especially if cations are present at high concentration, they can be complexed by the active site, even if they have a lower affinity for the active site than Pd(II).

We selected the best choice, firstly verifying that the use of Palladium standard solution and a multi-standard solution containing almost equal amount of Pd, Os, Ir, Pt, Ru and Rh gave spectra of the solid phase with no significant variations, neither at pH 1 or 0. This test has the limited value since it demonstrates that there is not significant interference coming from other precious metal ions.

So in a second test, we added in two separate systems of Pd-TazoC-Mar@ already at equilibrium at pH=0 and pH=1, Al(III) and Mn(II) 10 and 30 times more concentrated with respect to Pd(II). Only in the experiments at pH=0 we registered unmodified spectra for both concentrations, so we decided that pH=0 is the best choice to perform analysis on real

samples. It is worth to note that Al(III) and Mn(II) in the reference material here used for the method validation, are even more concentrate with respect to any of Pd(II) addition we did for the test, and even if their speciation in the final sample is not known, they had no influence in Pd(II) determination.

#### 4. Conclusions

We built up a cheap, extremely selective, optical device for Pd(II) sensing and quantification. Using an old ligand fixed on a solid, although obtaining disturbed vis signals registered in solid phase, we demonstrated that, with a proper tool, PLS, we obtained an analytical response which is reliable. The method is validated on certified samples, and has extremely low LOD and LOQ.

The idea to extract good quality information from rough signals opens a paramount number of applications on optical sensors, which often suffer of low performance. This is particularly true when the concern is not simply the sensing, but the quantification of one, or more than one, species.

#### Conflicts of interest

There are no conflicts to declare.

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