Electronic Supplementary Information (ESI)

of the paper of New Journal of Chemistry and titled

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

by:

Raffaela Biesuz, Valeria Marina Nurchi, Joanna Izabela Lachowicz and Giancarla Alberti.

Chapter S1 –Preliminary studies [moved from the text and adapted]

The spectra were collected with different mixture of the three metal ions, on the basis of a precise design of experiments, see R. Brerenton, *Analyst*, 1997, **122**, 1521-1522, to guarantee the construction of an equilibrated non correlated matrix. 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 Table S2). The validation step was successful only for Pd(II) and partially for Cu(II), (see Figures from S3 a to S5 b).

The unsatisfactory result was 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 S6, 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. Indeed, to evaluate in an unknown sample, the concentration of each analyte, from a spectra which is the sum of all the different contribution, the response of each of them, in terms of sensitivity, must be similar, which is not the case here.

Furthermore, other problems arose when we supposed to carry out the external validation test, a fundamental step in PLS modelling. Very few reference materials for Pd(II) can be found, being one the "Road Dust, trace elements, BCR 723" (Table S1 for the declared composition) 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 10^6 times more concentrated. All of these cations, at larger or lesser extension at pH = 4.5 are complexed by TazoC-Mar@, making the Pd(II) determination impossible.
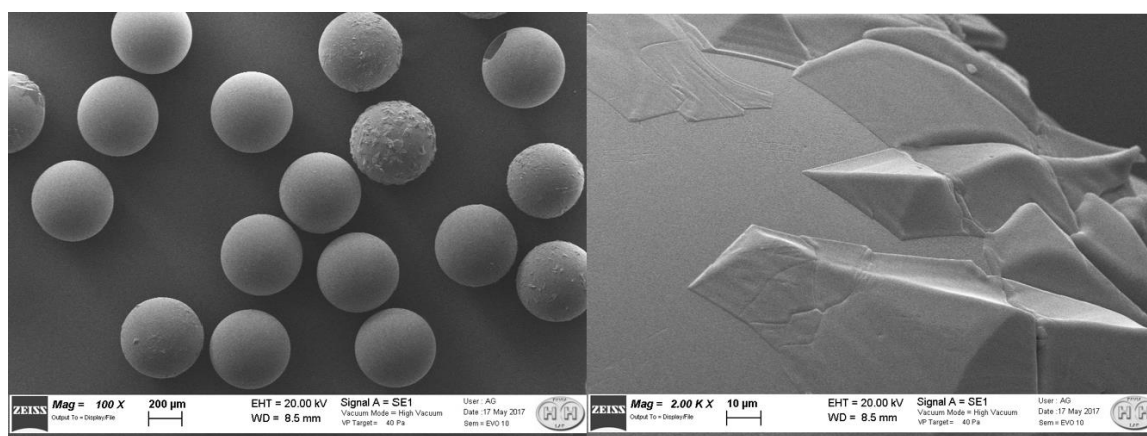
2. Figures of ESI

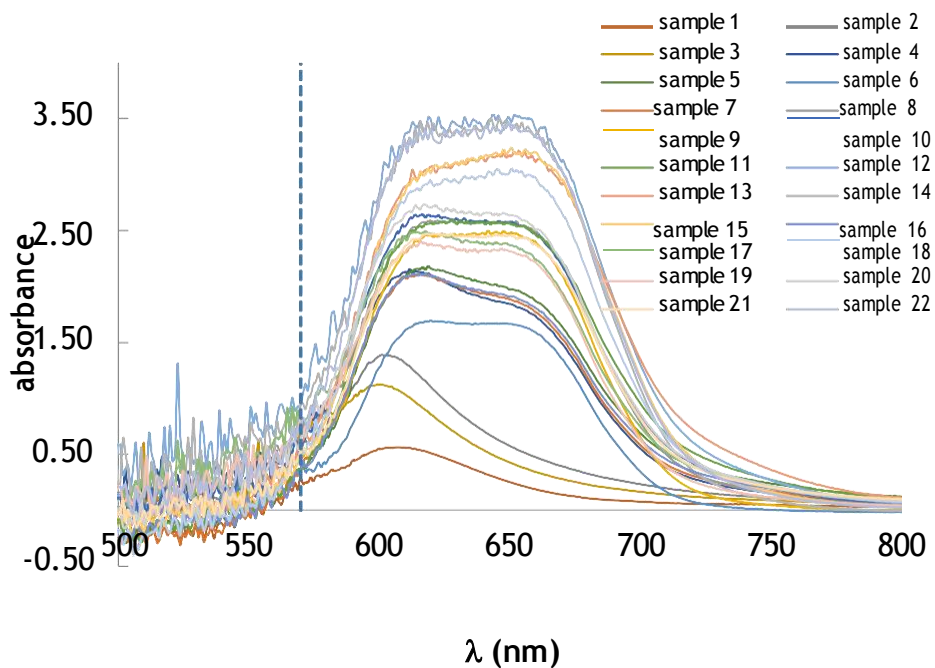**Figure S1** - SEM imagines of Marathon at different magnification

Figure S2 - Vis spectra of the samples built according to composition of table S2. V=20 mL, pH=4.5 and around 0.5 g of TazoC_Mar@. The data used for PLS are from λ 570 to 800 nm.
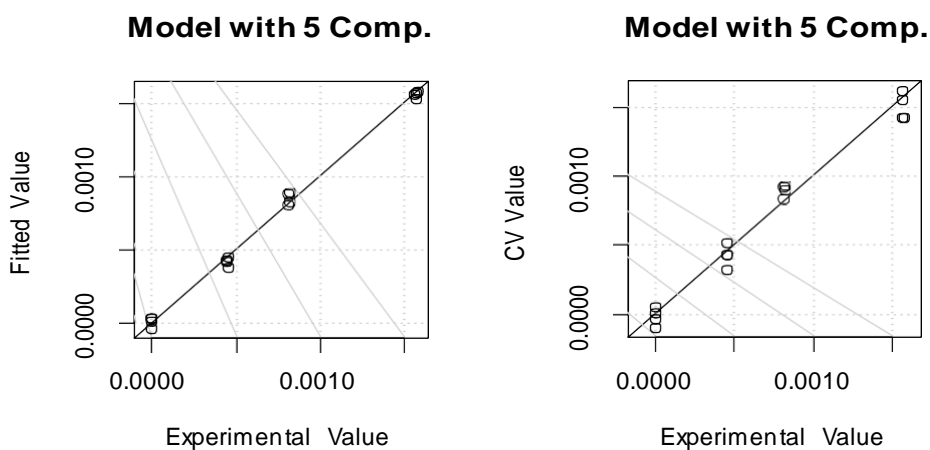

Figure S3 a
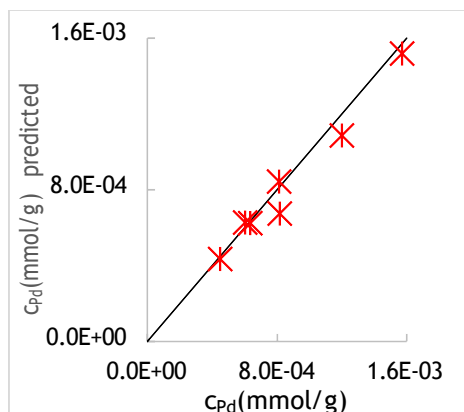The best model obtained for Pd(II) on data reported in Figure S2, pH=4.5.

Figure S3 b
Validation of the PLS model for Pd(II) at pH=4.5, with an external data set.

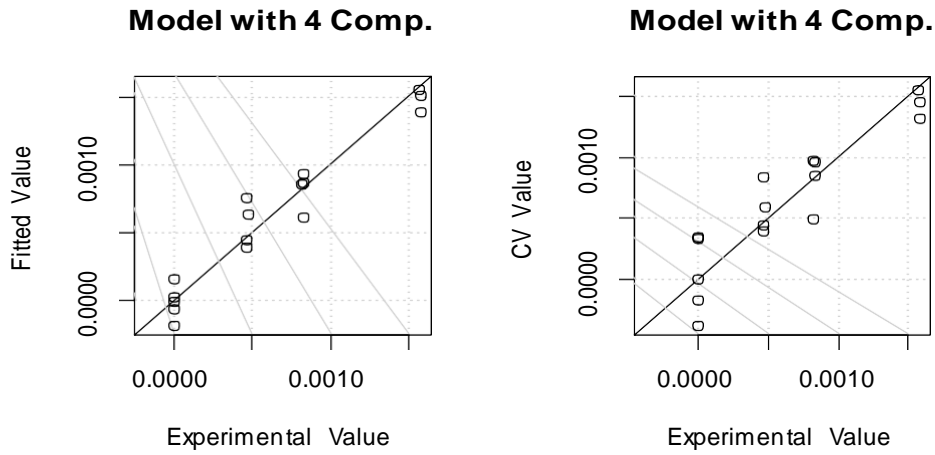**Model with 4 Comp.**

Model with 4 Comp.

Figure S4 a
The best model obtained for Cu(II) on data reported in Figure S2, pH=4.5.
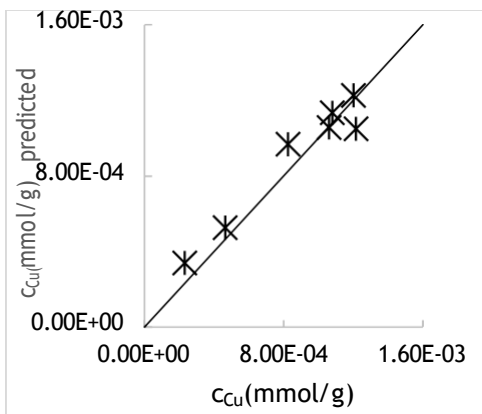
Figure S4 b
Validation of the PLS model for Cu(II) at pH=4.5, with an external data set.

Model with 2 Comp.

Model with 2 Comp.

Figure S5 a
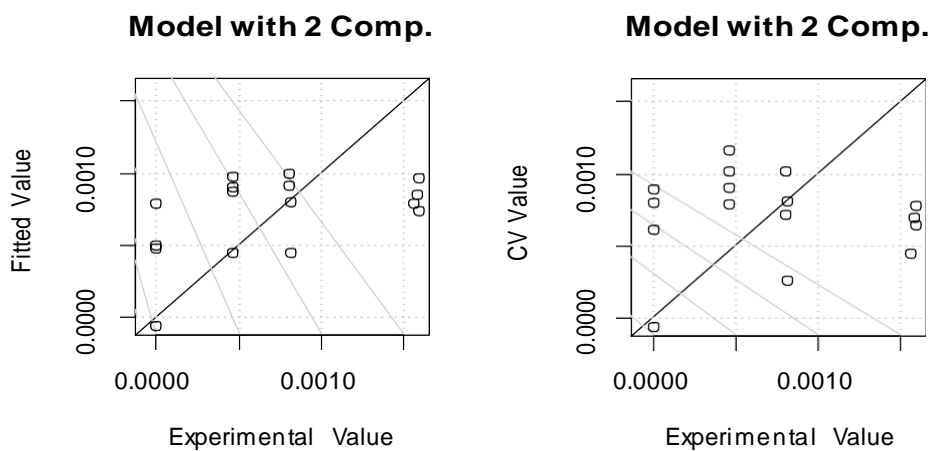The best model obtained for Ni(II) on data reported in Figure S2 at pH=4.5
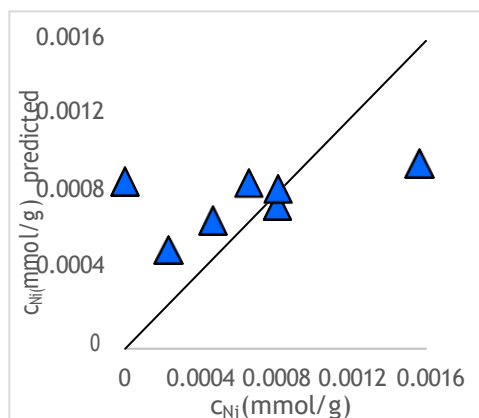
Figure S5 b
Validation of the PLS model for Ni(II) at pH=4.5, with an external data set.
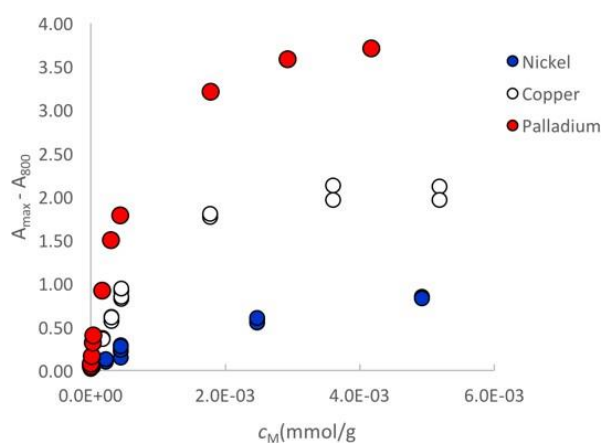
Figure S6 - Absorbance of the solid phase at the maximum wavelength of the complex at pH=4.5, V=20 mL, 0.5 g of TazoC-Mar@ after equilibration with increasing cation concentrations. Pd(II), red circles, Cu(II), white circles, Ni(II), blue circles.
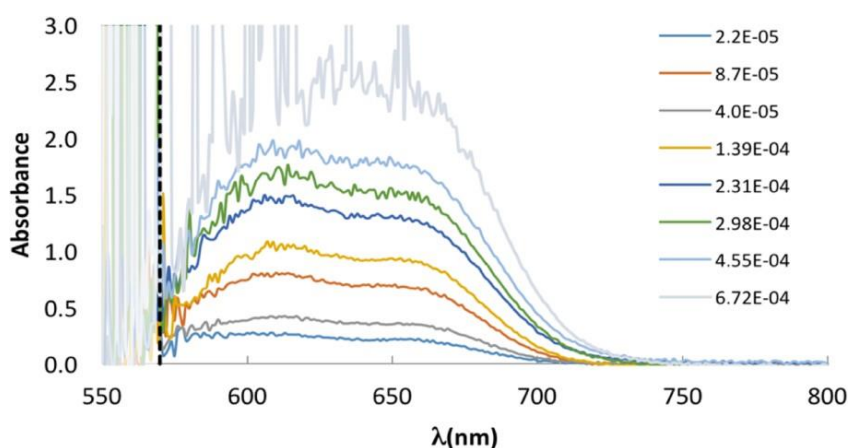
Figure S7 – Vis spectra of suspended TazoC-Mar@ in HNO_3 0.1 M, as function of increasing concentrations of Pd(II), as reported in the caption. Here the Pd(II) concentrations are referred to the solid phase (mmo/g). The blank is TazoC-Mar@ suspended in HNO_3 0.1 M without Pd(II).

Figure S8 – The dose response curve using univariate data treatment, achieved from spectra reported in figure S7. Net absorbance at λ=610nm is plotted vs the concentration of Pd(II) in the solid phase. The straight line was obtained by linear regression on the first 6 points, the second order equation reported in red was obtained performing a non-linear regression considering all the points.

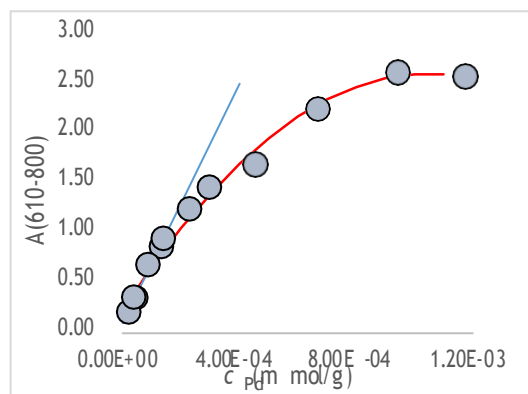## 3. Tables of ESI

Table S1 Reference material used for validation, BCR 723. In the first column the certificate composition is reported. Dissolving 0.3 g of sample in V=25mL, in columns 4, 5, 6, the final theoretical concentrations are reported.

	certificate	mg/g	PA	mg/L	µg/L	M
Pd(μg/Kg)	6.1	$6.10\ 10^{-06}$	106.42	$7.4\ 10^{-05}$	0.07	$7\ 10^{-10}$
Pt(μg/kg)	81.3	$8.13\ 10^{-05}$	195.078	$9.8\ 10^{-04}$	0.98	$5\ 10^{-09}$
Rh(μg/kg)	12.8	$1.28\ 10^{-05}$	102.9	$1.5\ 10^{-04}$	0.15	$2\ 10^{-09}$
Mn(g/kg)	1.28	1.28	55	15	15442	$3\ 10^{-04}$
Pb(mg/kg)	866	0.866	207	10	10447	$5\ 10^{-05}$
V(mg/kg)	75	0.075	51	1	905	$2\ 10^{-05}$
Hf(mg/kg)	2.2	0.0022	178.49	0	27	$1\ 10^{-07}$
Th(mg/kg)	4.8	0.0048	232.038	0	58	$2\ 10^{-07}$
Al %	3.75	11.31	27	136	136444	$5\ 10^{-03}$
Fe%	3.29	9.92264	55.8	120	119707	$2\ 10^{-03}$

Table S2

Plan of experiments according to Multilevel Partial Factorial Design (MPFD) considering 3 variables at 5 concentration levels, originally proposed for simultaneous determination of Pd(II), Ni(II) and Cu(II) at pH=4.5. See R. Brerenton, *Analyst*, 1997, **122**, 1521-1522

	Pd(II) (mmol/g)	Ni(II) (mmol/g)	Cu(II) (mmol/g)
sample 1	0	$1.56\ 10^{-03}$	0
sample 2	0	$4.65\ 10^{-04}$	$8.25\ 10^{-04}$
sample 3	0	$8.08\ 10^{-04}$	$4.63\ 10^{-04}$
sample 4	$4.48\ 10^{-04}$	$4.64\ 10^{-04}$	$4.65\ 10^{-04}$
sample 5	$4.51\ 10^{-04}$	$1.59\ 10^{-03}$	$1.58\ 10^{-03}$
sample 6	$4.48\ 10^{-04}$	0	0
sample 7	$4.51\ 10^{-04}$	$8.15\ 10^{-04}$	$8.27\ 10^{-04}$
sample 8	$8.15\ 10^{-04}$	$1.59\ 10^{-03}$	$4.68\ 10^{-04}$

sample 9	8.11×10^{-04}	8.11×10^{-04}	0
sample 10	8.16×10^{-04}	0	8.27×10^{-04}
sample 11	8.14×10^{-04}	4.65×10^{-04}	1.58×10^{-03}
sample 12	1.57×10^{-03}	1.58×10^{-03}	8.20×10^{-04}
sample 13	1.57×10^{-03}	8.08×10^{-04}	1.57×10^{-03}
sample 14	1.58×10^{-03}	4.63×10^{-04}	0
sample 15	1.56×10^{-03}	0	4.59×10^{-04}
sample 16	4.48×10^{-04}	0	1.08×10^{-03}
sample 17	6.32×10^{-04}	1.56×10^{-03}	1.06×10^{-03}
sample 18	1.20×10^{-03}	4.65×10^{-04}	8.25×10^{-04}
sample 19	6.38×10^{-04}	8.08×10^{-04}	4.63×10^{-04}
sample 20	8.11×10^{-04}	8.11×10^{-04}	1.22×10^{-03}
sample 21	8.16×10^{-04}	6.60×10^{-04}	8.27×10^{-04}
sample 22	1.57×10^{-03}	2.30×10^{-04}	2.31×10^{-04}

Table S3

The parameters for the regressions of data reported in figure 7, and S7 in the two different experimental conditions, HNO_3 1.0 M and 0.1M in the case of the straight line and the second degree equation.

Excel linear regression output for: y = bx+a

		case of 1.0M HNO_3		case of 0.1 M HNO_3	
param x	intercept	5260	0.24	6012	0.10
err par x	err. inter	543	0.07	368	0.03
R^2	err. on Y	0.9691	0.0931	0.9852	0.0414
F	df	94	3	267	4
$\Sigma RegQ$	$\Sigma ResQ$	0.815	0.026	0.458	0.007

Excel linear regression output for: y = cx^2+bx+a

			case of 1.0M HNO_3			case of 0.1 M HNO_3		
param x^2	param x	intecept	-3.11×10^6	5385	0.282	-2.17×10^6	4538	0.232
err par x^2	err par x	err. Inter.	2.7×10^5	308	0.064	2.6×10^5	301	0.053
R^2		err. on Y	0.9874	0.1047		0.9891	0.0993	
F		df	352	9		407	9	
$\Sigma RegQ$		$\Sigma ResQ$	7.716	0.099		8.021	0.089	

Table S4

The table produced by the software and the first graphical output, being the subsequent that reported in fig.7

CV% Explained Variance	1 comps	2 comps	3 comps	4 comps	5 comps
	88.77	93.01	95.63	95.59	95.57
RMSECV	1 comps	2 comps	3 comps	4 comps	5 comps
	1.52E-06	1.20E-06	9.46E-07	9.51E-07	9.53E-07

Minimum value found at component n.: 3

Model created with 3 components and saved in PLS object