1 **Monitoring dissolved orthophosphate in a struvite precipitation reactor with a voltammetric**

2 **electronic tongue.**

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11
12 **Abstract**

13 This study demonstrates the feasibility of using a voltammetric electronic tongue to monitor effluent dissolved

14 orthophosphate concentration in a struvite precipitation reactor. The electrochemical response of the electronic tongue

15 to the presence of orthophosphate in samples collected from the effluent of the precipitation reactor is used to predict

16 orthophosphate concentration via a statistical model based on Partial Least Squares (PLS) Regression. PLS predictions

17 were suitable for this monitoring application in which precipitation efficiencies higher than 80% (i.e., effluent dissolved

18 orthophosphate concentrations lower than 40 mg P-PO$_4^{3-}$) could be considered as indicator of good process

19 performance. The electronic tongue consisted of a set of metallic (noble and non-noble) electrodes housed inside a

20 stainless steel cylinder which was used as the body of the electronic tongue system. Fouling problems were prevented

21 via a simple mechanical polishing of the electrodes. The measurement of each sample with the electronic tongue was

22 done in less than 3 seconds. Conductivity of the samples only affected the electronic tongue marginally, being the main

23 electrochemical response due to the orthophosphate concentration in the samples. Copper, silver, iridium and rhodium

24 were the electrodes that exhibited noticeable response correlated with the dissolved orthophosphate concentration

25 variations, while gold, platinum and especially cobalt and nickel were the less useful electrodes for this application.

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27 **Keywords** electronic tongue; monitoring; orthophosphate; PLS; struvite precipitation

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1   INTRODUCTION

2   Phosphorus is the limiting nutrient for biological growth in most continental water bodies and its

3   input from wastewaters promotes eutrophication, an adverse response of the ecosystem

4   characterized by an accelerated plant and algal growth [1]. Although phosphorus can be removed

5   from wastewaters by chemical precipitation and/or biological processes, the application of

6   technologies for phosphorus recovery is of major interest since this nutrient is a non-renewable

7   resource essential for modern agriculture. Phosphorus peak was estimated to occur by 2035, after

8   which its demand would outstrip supply [2]. Approximately 17% of the total phosphorus in

9   phosphate rock mined specifically for food production is lost in human excreta via wastewater,

10   mainly in urine [3].

11

12   In this context, phosphate recovery from urine is an attractive choice, because phosphorus is present

13   in inorganic form, it is not bonded to the organic matter and urine represents only 1% of the total

14   volume of wastewater while contains up to 50 % of the total phosphate load in municipal

15   wastewaters [4]. Although different technologies can be used to recover phosphorus from urine,

16   chemical precipitation in the form of minerals with direct application to agriculture such as struvite

17   $(MgNH_4PO_4 \cdot 6H_2O)$ is being intensively studied by the scientist community [5-7]. In a struvite

18   precipitation reactor, it is important to timely detect poor precipitation conditions and when

19   experimental conditions should be changed. This can be done by measuring the key indicator of

20   process efficiency, i.e. orthophosphate concentration, in the effluent of the precipitation reactor.

21

22   In modern water and wastewater treatment processes, adequate instrumentation for on-line

23   monitoring, control and automation is essential for product quality, cost-effective and safe process

24   operation [8]. Instrumentation technology in the wastewater treatment field has evolved rapidly in

25   the last two decades increasing the opportunities of applying on-line process control to the variables

26   directly involved in process performance. However, the operation and maintenance of some nutrient

analyzers are tedious and time consuming, limiting their applicability [9]. Nutrient sensors include advanced analysis and have to be maintained and checked according to specific quality maintenance programmes to ensure the measurement quality [8]. In the context of orthophosphate monitoring, its concentration can be measured by conventional laboratory analytical procedures [10] or by analysers usually based on the molybdate-vanadate colorimetric method. Although analysers provide an almost continuous measurement (response time 5-10 minutes), they require operator maintenance and reagent consumption.

Another approach based on simple cobalt electrodes working in potentiometric mode have been reported to produce satisfactory performance in measuring phosphorus concentration. This concept was earliest introduced by Xiao [11], proposing a ion-sensitive electrode based on a surface modified cobalt as a phosphate-sensitive electrode material and suggested the oxidized surfaces of the metallic cobalt to be the responsible of the relatively selective potentiometric response towards phosphate. Different developments and applications ranging from monitoring phosphate in the microbial flocs of a bioreactor operated for enhanced biological phosphorus removal to phosphate measuring in lake water and sediment samples, or in biodiesel samples, cover recent references. [12-14] However, despite the developments made in this field, there is still significant interference in phosphate sensing [15].

As an alternative to conventional procedures and analysers, electronic tongues have emerged as a rapid, low-cost and simple tool for liquid analysis. The strategy of electronic tongues relies on the use of semi-specific sensors that produce a signal pattern when inserted in the liquid sample that can be related to either a specific compound or a quality aspect, processing the signal pattern with chemometric techniques [16]. They have been applied in a wide range of applications, such as in food industry, environmental analysis, water quality monitoring including wastewater characterization [17-22]. Voltammetric tongues (i.e., electronic tongues in which a potential is

1   applied and the resulting current is measured) are more versatile and robust than potentiometric

2   tongues since they are usually less influenced by electrical disturbances and have a favourable

3   signal to noise ratio [23].

4

5   Based on our previous research [16, 24] and following our interest in the design of different sensing

6   systems we report herein a new application of a voltammetric electronic tongue: monitoring

7   dissolved orthophosphate in a lab-scale struvite precipitation reactor. The electronic tongue

8   consisted of a set of metallic (noble and non-noble: iridium, rhodium, platinum, gold, silver, cobalt,

9   copper and nickel) electrodes housed inside a stainless steel cylinder which was used as the body of

10   the electronic tongue system. Different waveforms for the electrodes designed in our prior research

11   are compared.

12

13   **MATERIALS AND METHODS**

14   **Experimental set-up**

15   Figure 1 shows a scheme of the pilot plant used in our struvite ($MgNH_4PO_4 \cdot 6H_2O$) precipitation

16   studies [25, 26]. In these studies parameters such as pH, temperature, stirring speed and ions ratios

17   are varied to optimize the precipitation process. As can be seen in Figure 1, the pilot plant consist in

18   a glass stirred precipitation reactor (22.88 L of volume) equipped with three pumps for influent

19   (synthetic urine), magnesium source and sodium hydroxide (for pH control) dosing through three

20   independent stainless steel injection tubes, and two balances to monitor the magnesium and sodium

21   hydroxide flows. The precipitation reactor is divided into two parts: the reaction zone (4.95 L in the

22   bottom part), designed according to the typical dimensions of a perfectly mixed reactor and the top

23   part which is the settling zone (17.94 L), that prevents fine particles from being lost with the

24   effluent. A detailed description of the pilot plant can be seen in [25].

25

26   **[Place Figure 1 near here]**

1

The influent used in the struvite precipitation studies (see Figure 1) reproduce the ions concentrations observed in urine stored for 3 days [26] and diluted according to the typical dilution rate in no-mix toilets (1:4). In these precipitation studies it is important to know the dissolved orthophosphate concentration in the effluent, which can vary from 0 mg/L (indicating the best possible precipitation results, i.e. 100% precipitation efficiency, since no dissolved orthophosphate is lost with the effluent) to the concentration of this compound the influent (196 mg P-PO$_4^{3-}$, reflecting that none of the orthophosphate in urine is being precipitated). In this context, precipitation efficiencies higher than 80% (i.e., dissolved orthophosphate concentrations lower than 40 mg P-PO$_4^{3-}$) could be considered as indicator of good process performance. Therefore, fast prediction dissolved orthophosphate concentration is valuable for tracking the evolution of the precipitation process and to reduce the time response between process failure and operator actuation.

Electronic tongue

The electronic tongue used in this work is based on pulse voltammetry and was developed by the Instituto Interuniversitario de Reconocimiento Molecular y Desarrollo Tecnológico (IDM) at the Universitat Politècnica de València (UPV). It consists on an electronic equipment, a software application that runs on a PC, and eight metallic electrodes (four noble metals: iridium, rhodium, platinum and gold; and four non-noble metals: silver, cobalt, copper and nickel). The working electrodes were housed in a stainless steel cylinder that served also as auxiliary electrode (i.e., counter-electrode) and a saturated calomel electrode was used as reference electrode. The electronic equipment applies a set of voltage pulses to the working electrodes and measures the generated current (i.e., the electrochemical response). To prevent fouling problems, the working electrodes were manually polished. Prior to starting the measurements, each electrode surface was prepared by mechanical polishing with an emery paper, and rinsed with distilled water. Afterwards it was

1 polished on a felt pad with 0.05 mm alumina polish from BASi^{TM}, washed with distilled water and

2 polished again on a nylon pad with 15, 3 and 1 mm diamond polishes, to produce a smooth, mirror-

3 like electrode surface. Finally, during the experimental measurements a simple diamond polishing

4 was manually applied to each working electrode followed by washing with distilled water after each

5 measurement. Auxiliary and reference electrodes were only rinsed with distilled water. A detailed

6 description of the electronic tongue can be found in [24].

7

8 In this study two different pulse sequences (named generic and specific) determined by cyclic

9 voltammetry were used and compared in terms of dissolved orthophosphate concentration

10 prediction. The generic pulse sequence applies the same set of voltage pulses (see Figure 2a) to the

11 eight electrodes and was determined as explained in Campos *et al.* [24]. This pulse sequence was

12 designed to quantify a variety of compounds (sulphate, bicarbonate, acetate, ammonium,

13 orthophosphate, etc in aqueous solutions) applying the same voltage pattern to all the electrodes.

14 The specific pulse sequence (determined as explained in Campos *et al.*, [16]) applies a different set

15 of voltage pulses for each non-noble electrode (Figures 2c to 2f) and the same set of pulses to the 4

16 noble electrodes (Figure 2b). This pulse sequence was designed to quantify specifically two

17 nutrients: ammonium and orthophosphate.

18

19 **[Place Figure 2 near here]**

20

21 **Orthophosphate concentration measurement procedure**

22 Grab samples from the precipitation reactor effluent were analysed for dissolved orthophosphate

23 concentration (P-PO$_4^{3-}$). The sample was immediately filtered through a 0,45 µm size pore filter,

24 and then orthophosphate concentration (P-PO$_4^{3-}$) was determined by conventional laboratory

25 analytical methods (in accordance with Standard Methods [9]). Afterwards, the sample was split

26 into two equally aliquots:

- In the first aliquot, the electrochemical response of the sample was measured with the electronic tongue at room temperature (20 ± 2 ℃). The required time to complete the measurement was less than 3 seconds. The rate limiting step for the data acquisition was the mechanical polishing of the electrodes which required about 5 minutes. Two different pulse sequences were applied: generic pulse sequence and specific pulse sequence. In both cases the electrochemical response of the 8 electrodes to the pulse sequence applied in the sample was recorded. In the generic pulse sequence, a total of 8000 values of electric current (µA) (100 values recorded per pulse $\times$ 10 pulses $\times$ 8 electrodes) were recorded for each sample. In the specific pulse sequence a total of 7968 electric current (µA) values (83 values recorded per pulse $\times$12 pulses $\times$ 8 electrodes) were recorded for each sample.

- In the second aliquot, the conductivity of the sample was increased to 9000 µS/cm (dosing potassium nitrate: KNO_3, as solid powder with high purity grade ($> 99,9\%$)), and afterwards the electrochemical response of the sample was measured with the electronic tongue (exactly as with the first aliquot). Conductivity correction was done to determine if the electronic tongue response was due either to the different conductivity of the samples, or to the different orthophosphate concentration, or to both effects.

Following this procedure a total of 78 samples were measured.

Partial Least Squares Modelling

Partial Least Square (PLS) regression is a multivariate statistical projection method, widely used in chemometrics to relate two data matrices (X and Y) while compressing high-dimensional data into a lower-dimensional space. This technique aims at predicting Y from X-variables, by simultaneous decomposition of both matrices into a group of new independent variables (latent variables or components) which maximize the covariance between both X and Y [27].

X matrix was composed by the electrochemical response of the 8 electrodes to the pulse sequence applied in all samples, and the Y vector were the dissolved $P-PO_4^{3-}$ concentrations in all samples determined by the conventional analytical method in laboratory. Therefore, the Y-vector has the value of one variable (dissolved $P-PO_4^{3-}$ concentration) in the 78 samples, while the X-matrix in the generic pulse sequence has 8000 variables (10 pulses applied per electrode $\times$ 100 values of electric current recorded per pulse $\times$ 8 electrodes) in the 78 samples, and 7968 variables in the specific pulse sequence (12 pulses applied per electrode $\times$ 83 values of electric current recorded per pulse $\times$ 8 electrodes).

From the 78 samples collected from the effluent of the struvite precipitation reactor, 52 were used for PLS model calibration, and 26 samples for model validation. To be precise one out of every three samples was selected for validation purposes. Models were built on pre-processed data (mean-centered and scaled to unit variance). Cross-validation was used to determine the optimal number of latent variables in the model calibration stage. Model evaluation was carried out in the validation data set comparing laboratory measurements versus PLS predicted concentrations using the correlation coefficient (R^2), the line parameters p_1, p_2 (from $y = p_1 x + p_2$ in the lineal regression model of lab-measured versus PLS predicted values) and the root mean square error of prediction (RMSEP).

Software

Two software packages have been used in this work: MATLAB 7.7 and SIMCA-P 9.0.

RESULTS AND DISCUSSION

Figure 3 shows the performance of the Partial Least Squares (PLS) models developed using the electrochemical response of the eight electrodes to predict dissolved phosphorus concentration in the effluent of the struvite precipitation reactor. In each graph, the perfect fit (line with slope 1:1

1   and y-intercept 0) is included as solid line to enable a graphical comparison with each PLS model

2   fit (dashed line) of the validation data set. Two additional parameters are also included to assess

3   each PLS model performance: the correlation coefficient and root mean square error of the

4   prediction data set (RMSEP) (see Figure 3). The number of statistically significant components

5   according to cross-validation was six in these PLS models. The PLS model should exhibit a balance

6   between fit and prediction performance. Since the goodness of fit, parameter quantified by the

7   explained variation parameter (R^2), increases with model complexity (the higher the number of

8   latent variables the higher the R^2 parameter), and the goodness of prediction parameter (Q^2,

9   predicted variation) was used to determine if a new latent variable must be retained in the model.

10   Essentially cross-validation procedure was applied in the following way: the calibration data was

11   divided into seven groups. A PLS model was developed for all except one group, which was used as

12   a test set to assess the prediction performance of the model (i.e., the SEP is calculated for that group

13   no used for PLS model establishment). This procedure was repeated seven times (as the calibration

14   data was divided into seven groups), and all the SEP values were summed to obtain an overall SEP-

15   value. If a new PLS component improved the prediction capability in comparison with the previous

16   PLS component, then, the new component was retained in the model.

17

18   The graphs of Figure 3 display the measured versus PLS predicted values of dissolved phosphorus

19   concentration based on the electronic tongue using the specific pulse sequence and the generic pulse

20   sequence. The measured versus PLS predicted values of dissolved phosphorus concentration are

21   plotted for both, data without modifying the conductivity of the samples and data for which the

22   conductivity was increased to 9000 µS/cm. In all cases, data shown include 52 training samples and

23   the 26 validation samples.

24

25   **[Place Figure 3 near here]**

26

1   As can be seen in Figure 3 an adequate fit was obtained in all models irrespective of the pulse

2   sequence applied. PLS models developed using the electrochemical response from the samples with

3   the same conductivity (i.e., samples in which the conductivity was increased to 9000 µS/cm as

4   described in the material and methods section), show only a minor decline in performance (slight

5   increase in RMSEP and slight decrease in R^2) in contrast with those models that used the response

6   from samples with conductivity not modified. This result strongly suggests that the electronic

7   tongue response is mainly due to the different orthophosphate concentration in the samples and only

8   marginally to the conductivity.

9

10   In Figure 3 it can also be seen that the PLS models developed using the electrochemical response

11   from the specific pulse sequence exhibit better precision (i.e., lower RMSEP) and correlation, but

12   the slope of the fit deviates from the perfect fit (solid line with slope 1:1 and 0 y-intercept) more

13   than the PLS models that used the response of the generic pulse sequence. This deviation is clearly

14   due to the two samples with dissolved phosphorus concentration over 120 mg $P-PO_4^{3-} L^{-1}$ which the

15   PLS models developed using the response from the specific pulse sequence cannot adequately

16   predict. When these two validation samples are omitted to assess the performance of these PLS

17   models, the slope of the fit approaches to 1 and the RMSEP decreases (being 7.92 in the PLS model

18   that used the response from samples with no conductivity correction applied). It should be

19   highlighted that for monitoring dissolved orthophosphate in the struvite precipitation reactor, it is

20   not relevant to predict concentrations over 100 mg $P-PO_4^{3-} L^{-1}$ with high precision, since these

21   concentrations in the effluent would clearly indicate poor process performance (as precipitation

22   efficiencies would be lower than 50%). Indeed, concentrations over 40 mg $P-PO_4^{3-} L^{-1}$ would

23   require operator action to solve the inefficient process situation or experimental conditions changed

24   to improve the struvite precipitation efficiency.

25

The lower performance at high phosphorus concentration could be due to either a saturation of the electrodes or to insufficient training samples at high phosphorus concentrations (to allow the PLS model adequately represent these range of concentrations, i.e., 100-180 mg L^{-1}; note that most of the training samples exhibit concentrations lower than 60 mg L^{-1}) or to a measurement problem with that samples or to a combination of the reasons mentioned. To assess if these samples fitted the PLS model, the distance to the model in X space (Dmod-X) for the validation set was plotted (Figure 4a). As can be seen in this Figure one of the samples over 120 mg L^{-1} clearly exceeds the critical distance for the 0.01 probability level (i.e., 99% tolerance region) of the training samples, thus the model is warning that the electrochemical response for this validation sample clearly do not conform the correlation pattern captured by the PLS model developed with the training samples, and the prediction could be inadequate (as it was). Equally inadequate was the prediction of the other sample with high phosphorus concentration despite being almost on the critical distance. The prediction error in relation to dissolved phosphorus concentration with the 95% prediction interval is shown in Figure 4b, where it can be seen that there are positive and negative deviations and that the highest deviations occur in samples over 120 mg L^{-1}. Please note, that to calculate the deviation error, the measured phosphorus concentration is required, but not for the Dmod-X calculation which is only based in the electrochemical response of the electronic tongue, thus, providing in advance useful information on the reliability of the prediction.

[Place Figure 4 near here]

After analysing the performance of the different PLS models, it can be concluded that the specific pulse is preferred (as better precision is achieved) over the generic pulse and for practical application no conductivity correction should be applied. Predictions of this PLS model were adequate for this monitoring application in which precipitation efficiencies higher than 80% (i.e., dissolved orthophosphate concentrations lower than 40 mg P-PO$_4^{3-}$ L^{-1}) could be considered as

1   indicator of good process performance. Moreover, the electronic tongue offers a potential for

2   continuous in situ monitoring since the required time to complete the measurement was less than 3

3   seconds, reducing the time of traditional laboratory determination and allowing early detection of

4   process upsets and poor precipitation operational conditions. The rate limiting step for the data

5   acquisition was the mechanical polishing of the electrodes which required about 5 minutes.

6

7   Since the electronic tongue consists in a set of eight individual electrodes, it is interesting to analyse

8   their individual contribution to the global model performance. For this purpose, eight individual

9   PLS models to predict dissolved phosphorus concentration in the effluent of the precipitation

10   reactor were created. Each model is based on the electrochemical response of each electrode using

11   the specific pulse sequence on the samples without conductivity modification. Table 1 shows for

12   each PLS model, the number of latent variables for model development (i.e., training or calibration

13   stage) and the performance parameters for the validation data set. The models are arranged

14   according to ascending value of root mean square error of prediction (RMSEP). As can be seen in

15   Table 1, rhodium, copper, silver, and iridium were the electrodes that exhibited response noticeable

16   correlated with the dissolved orthophosphate concentration variations, allowing better predictions

17   (in terms of RMSEP and R^2 values) of this compound in the effluent of the struvite precipitation

18   reactor. On the other hand, platinum, gold and especially cobalt and nickel, were the less useful

19   electrodes for this application.

20

21   **[Place Table 1 near here]**

22

23   Finally, since orthophosphate is not an electroactive species, a new experiment was performed to

24   show the electrochemical response data with new samples lab-prepared, varying the orthophosphate

25   concentration. For this purpose, 1.5 litre synthetic sample with all urine components except

26   phosphate was prepared. Then, five 250 mL aliquots were taken, and in each sample a different

1 quantity of KH_2PO_4 (solid powder) was added, achieving different final concentrations of

2 orthophosphate in each sample: 0, 45.3, 100.9, 138.9 and 183.6 mg P-PO_4 L^{-1}, thus spanning the

3 range of possible orthophosphate concentrations in the effluent of the struvite precipitation reactor

4 (0 – 196 P-PO_4 mg L^{-1}). Afterwards, the electrochemical response of each sample was measured at

5 room temperature (20 ± 2ºC), using the specific pulse sequence, obtaining 7968 electric current

6 (µA) values per sample (83 values recorded per pulse x 12 pulses x 8 electrodes). After each

7 measurement the same simple diamond polishing was manually applied to each working electrode

8 followed by washing with distilled water after each measurement. Auxiliary and reference

9 electrodes were only rinsed with distilled water. The results are shown in Figure 5.

10

11   **[Place Figure 5 near here]**

12

13 As can be seen in Figure 5, the electric current values vary considerably (from -1320 to 2100 µA)

14 and do not allow to clearly appreciating the differences between samples with different

15 orthophosphate concentration. However, when parts of the electrodes response are zoomed in, it can

16 be seen that the response differs from sample to sample and it was also found that there are parts of

17 the electrodes response that exhibit the same trend of phosphate concentration (see for instance

18 Figure 5b, from Rhodium electrode), while in other cases, the response cannot be correlated with

19 orthophosphate (as Cobalt in Figure 5a, in which the highest orthophosphate concentration exhibits

20 an intermediate electric current in comparison with all samples). It is the objective of the partial

21 least square technique to find those electrical responses that correlate best with the compound of

22 interest (orthophosphate in this case), to obtain an accurate and consistent predictive model.

23

24 **CONCLUSIONS**

In this work, a method to monitor effluent dissolved orthophosphate in a struvite precipitation reactor based in the use of a voltammetric electronic tongue is proposed. The electronic tongue consisted of a set of metallic (noble and non-noble) electrodes housed inside a stainless steel cylinder which was used as the body of the electronic tongue system and served also as auxiliary electrode (i.e., counter-electrode) and a saturated calomel electrode that was used as reference electrode. The main conclusions that can be drawn from this study are:

- It is feasible the use of simple electronic tongues to monitor the orthophosphate concentration in the effluent of a struvite precipitation reactor.

- The electronic tongue offers a potential for continuous in situ monitoring of orthophosphate concentrations requiring less than 3 seconds to complete each measurement, reducing the time consuming analytical laboratory procedures, no requiring reagent consumption and allowing early detection process upsets and poor precipitation operational conditions.

- Applying a specific pulse designed to quantify specifically the pollutant of interest allow better precision in concentration predictions than a generic pulse able to quantify a variety of compounds.

- A high correlation between data from the electronic tongue and the concentration of orthophosphate was observed which is related to the differential electrochemical response of the set of electrodes in the presence of orthophosphate.

- Copper, silver, iridium and rhodium were the electrodes that exhibited electrochemnical response highly correlated with the dissolved orthophosphate concentration variations in the effluent of the precipitation reactor. Gold, platinum and especially cobalt and nickel were the less useful electrodes for this application.

- The main electrochemical response of the samples is due to the orthophosphate concentration in the samples, being the electronic tongue measurement only maginally affected by the conductivity of the samples.

1

2 The main action when high phosphate concentration would be found at the output of the struvite

3 precipitation reactor would be triggering a warning message to the plant operator. Then the plant

4 operator, could access to all data gathered in the PC from the pilot plant via Internet (if not at the

5 laboratory) to remotely identify the causes of the inefficient process situation, and act accordingly

6 to solve it. If the output phosphate concentration is too low, no operator action is required, because

7 it indicates high precipitation and recovery efficiencies.

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9 **ACKNOWLEDGEMENTS**

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1 **Table 1.** Number of latent variables and performance parameters for the 26 validation samples of the PLS models based

2 on the electrochemical response of each electrode obtained applying the specific pulse sequence on samples without

3 conductivity correction.

Electrode	N. Latent Variables	R^2	p1	p2	RMSEP
Rhodium	6	0.830	0.780	9.207	13.56
Copper	6	0.830	0.755	7.735	13.77
Silver	6	0.810	0.897	3.935	14.50
Iridium	6	0.770	0.779	9.381	15.63
Platinum	6	0.609	0.630	10.684	20.64
Gold	6*	0.348	0.412	27.344	26.95
Nickel	6*	0.001	0.008	32.769	33.65
Cobalt	6*	0.000	0.000	38.123	38.92

4 * The latent variables from these PLS models were not statistically significant according to cross-validation.
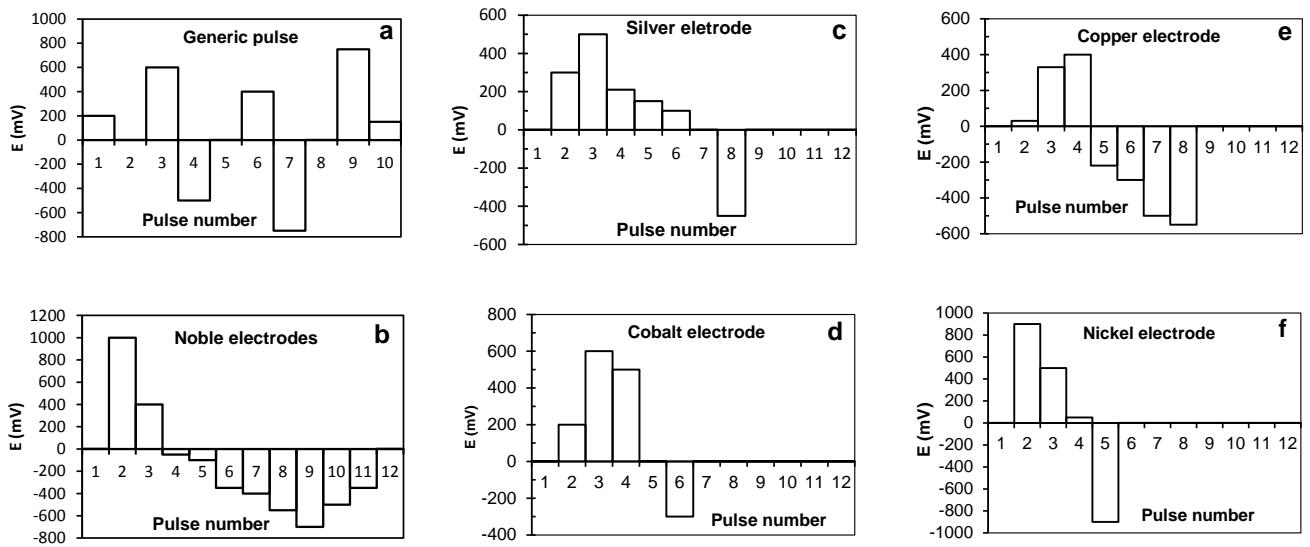
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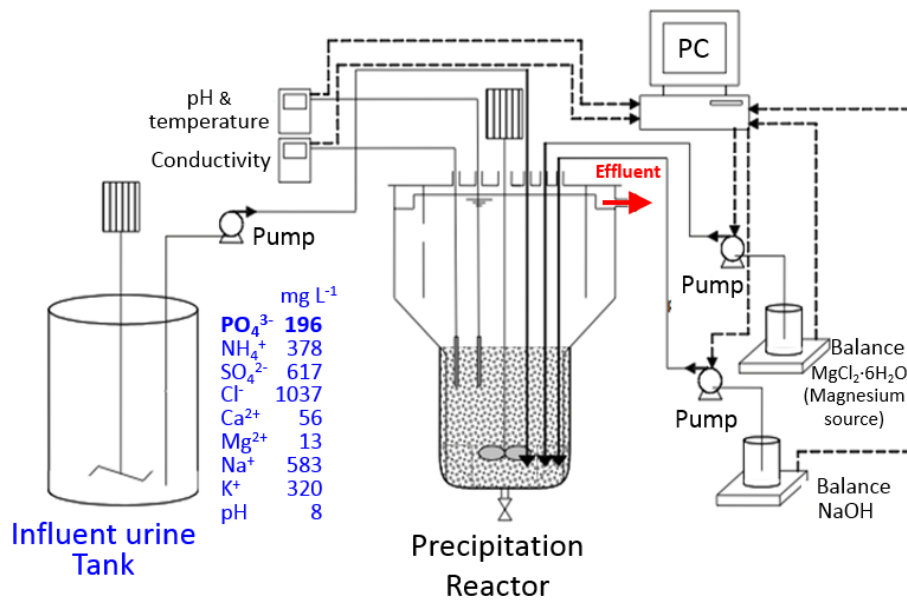
Figure 1. Scheme of the lab-scale struvite precipitation pilot plant. Composition of the synthetic urine influent (in blue) used in the study, and effluent of the precipitation reactor (in red) where samples were manually taken for orthophosphate concentration measurement.

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Figure 2. Applied pulse sequences used to obtain the electrochemical response of the electronic tongue to the presence

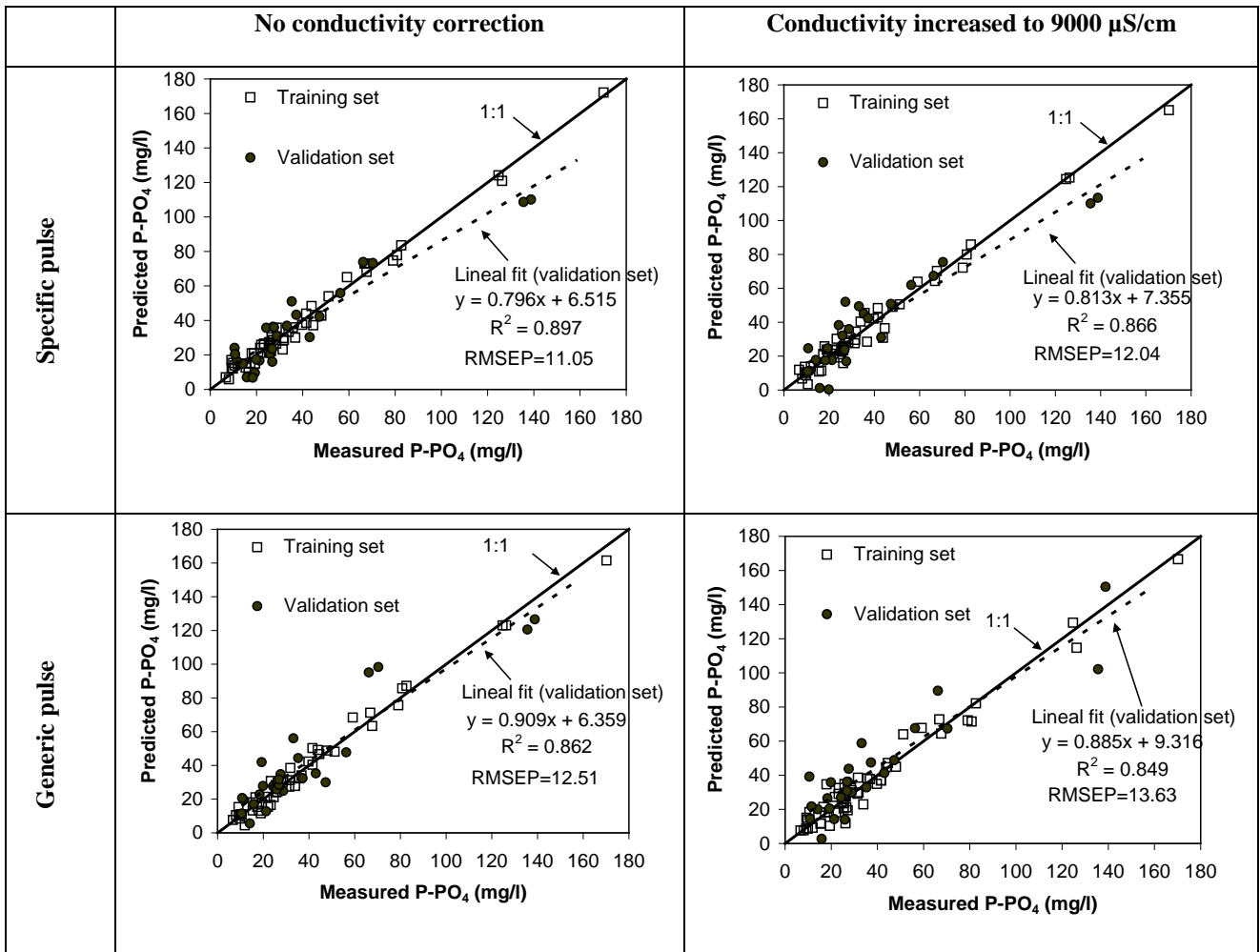of orthophosphate using (a) generic pulse and (b to f) specific pulse.

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Figure 3. Measured versus PLS predicted values of dissolved phosphorus concentration based on the electrochemical response of the 8 electrodes: using the specific pulse sequence (upper graphs), the generic pulse sequence (lower graphs), without modifying the conductivity of the samples (left graphs), increasing conductivity (right graphs). Data shown includes the 52 training samples and the 26 validation samples. The lineal fit is only based on the validation samples.

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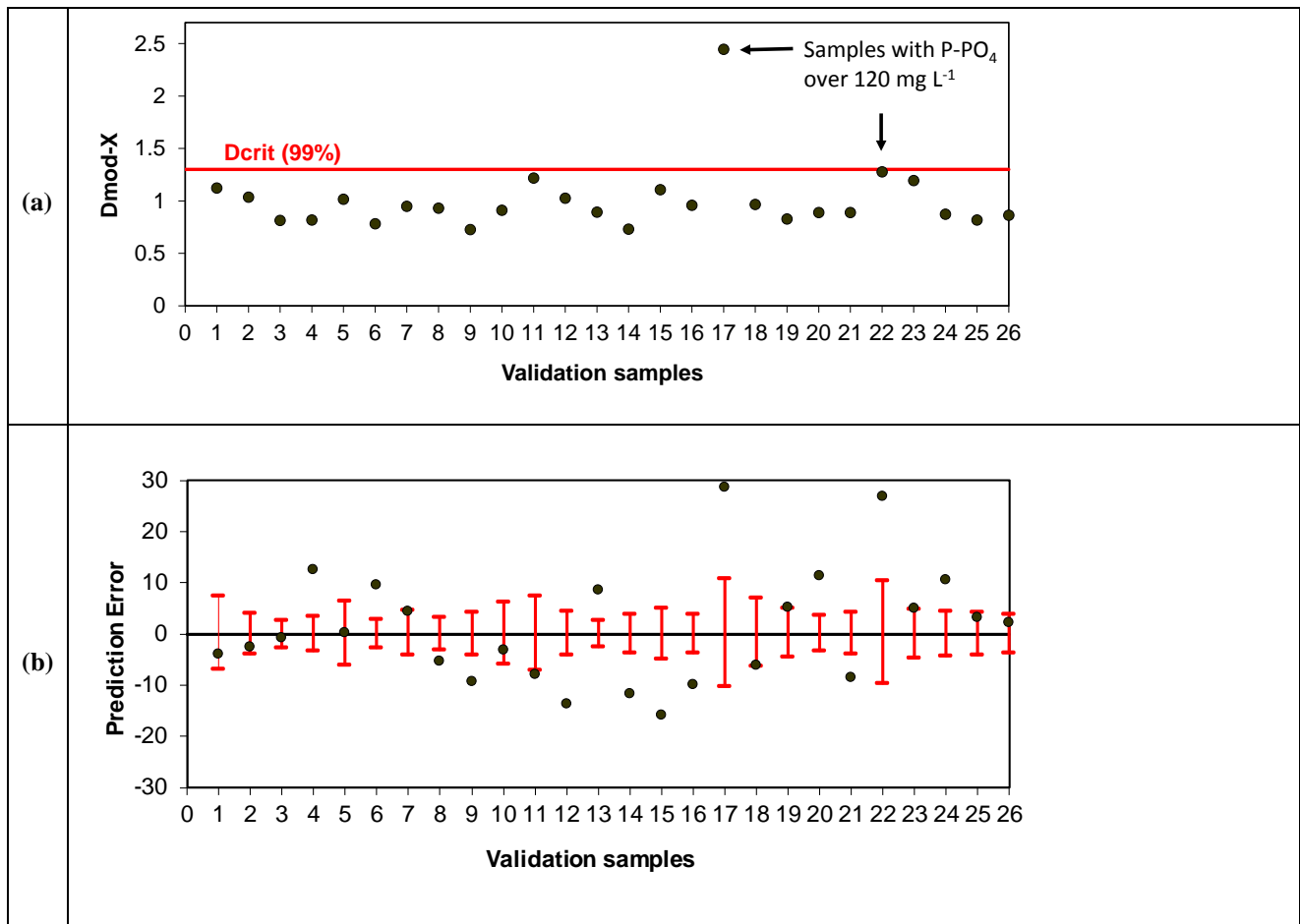
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3 **Figure 4. (a)** Distance to the model in X-space of the validation samples for the PLS model based on the

4 electrochemical response using the specific pulse sequence on the samples without conductivity modification. Critical

5 distance (Dcrit) defining the 99% tolerance region of the training samples. **(b)** Deviations, calculated as measured

6 minus PLS predicted values of dissolved phosphorus concentration, with the 95% prediction interval for each sample.
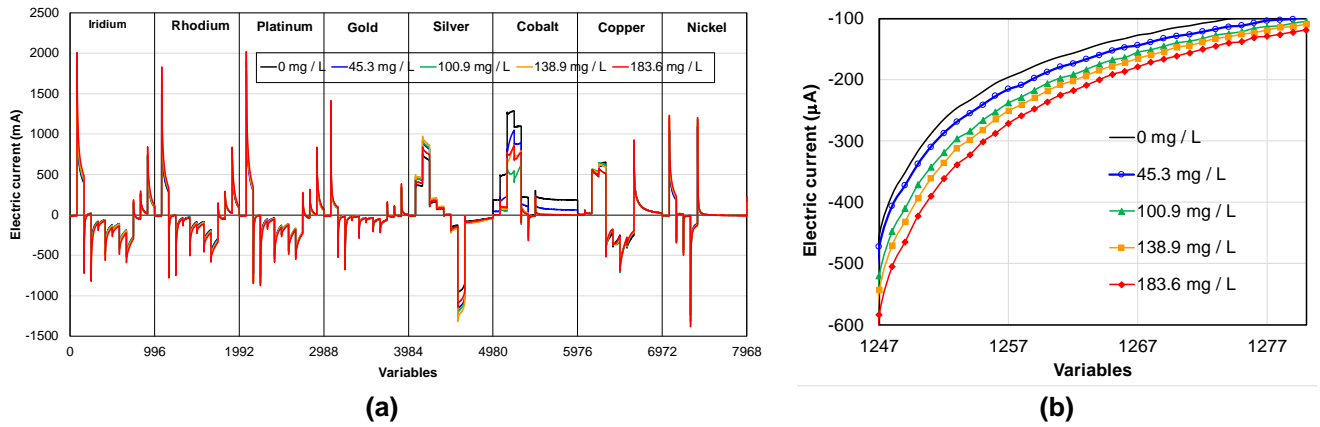
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2 New figure, added as recommended by the referee:
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(a)

(b)

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5 **Figure 5.** Electrochemical response using the specific pulse sequence on samples with increasing orthophosphate

6 concentration: **(a)** response from all electrodes **(b)** zoom in on a specific part of the Rhodium response, where it can be

7 clearly seen different electric current response for each sample.

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