

D 4.3 Sensors for orthophosphate analysis

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(D 4.3.1, D. 4.3.2, D. 4.3.3 & D 4.3.4)

Annex to the Progress Report VI
February 2022
Version n.1

PROJECT AdSWiM

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Work Package:	WP 4 - Innovative solutions in analytical, microbiological controls and to treat urban wastewaters (UWW)
Activity:	4.3 Innovative Analytical Methods/Devices (IAMD) Sensors for orthophosphate analysis
Phase Leader:	UNIUD
Deliverable:	D 4.3.1, D 4.3.2, D 4.3.3 & D 4.3.4

Version:	Final 1.0	Date:	March 2022
Type:	Report		
Availability:	Open		
Responsible Partner:	UniUD		
Editor:	Sabina Susmel		
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CONTENTS

***PART 1: INTRODUCTION AND STATE OF THE ART*..... 4**
D 4.3.14
 General objectives 5

***PARTE 2: PREPARATION OF THE COMPOSITE ELECTRODES AND CHARACTERIZATION*..... 5**
D 4.3.2 & D 4.3.35

2a_Preparation and characterization of plastic electrodes modified with ammonium heptamolybdate7

2b_Preparation and characterization of plastic electrodes modified with tetrabutyl ammoniumhexamolybdate9

2c_Preparation and characterization of plastic electrodes modified with with tetrabutyl ammonium octamolybdate11

2b_a_ Electrodes prepared from stock solutions of octamolybdate dissolved in acetonitrile .11

2_b_c_Electrodes prepared from stock solutions of octamolybdate dissolved in propylene carbonate14

2_c_ electrodes prepared by addition of nanoparticles mesoporous silica-based and octamolybdate16

PARTE 3: PERFORMANCES AND COMPARISON WITH OTHER ELECTRODES ... 17
D 4.3.417

References 17

PART 1: INTRODUCTION AND STATE OF THE ART

D 4.3.1

The northern Adriatic is the slope region from the Venice-Trieste shoreline to the line connecting Ancona on the Italian side of Zadar on the Croatian coast [1]. It is a semi-enclosed basin with limited water circulation and smoothly flow current being strongly influenced by fresh-water discharge from rivers (as Po in Veneto and Isonzo in Gulf of Trieste). Particularly, orthophosphate, the available form of phosphorous (P) is essential to all life forms, however, in high concentration induces eutrophication (10 ppb of orthophosphate is a concentration high enough) [2]. Excessive nutrients inflow of phosphorous as well as nitrogen, is typically consequence of industrial, agricultural or domestic waste runoff [3]. With the aim of environmental protection, water policies [2] set limits for nutrients including orthophosphate (i.e. 2 ppm in treated urban wastewater). However, oligotrophic conditions are now noticed in northern Adriatic. Recently Lazzari et al. (2016) detected orthophosphate concentrations in northern Adriatic below 2 ppb which is close to those values obtained at the Mediterranean sea [4]. The interesting fact is that the amount of nitrate is very high in comparison with Mediterranean sea, which means that a possible eutrophication process can happen if the orthophosphate concentration increase since this last one is the most important limiting nutrient for this oligotrophic system.

The gold standard method for orthophosphate quantification is based on the color change of a phosphomolybdate complex which is commonly known as molybdenum-blue method. The methodology involve the use of molybdate anions that in acid conditions and after 60 min of incubation form the phosphomolybdate complex:



This method is not practical for in field detection since the reaction between the molybdate anions (from a molybdate ion stock solution) and the orthophosphate happens in solution and involve an incubation step for at least 60 min. The main problems related to these methods are:

- Low sensitivity,
- Detection with all reagents in solution
- Low kinetic of complex formation
- Sensitive to sample turbidity

In addition, other problem is the difficulty to use them for in field detection of wastewater and seawater samples. In particular, for seawater samples, the sensitivity of molybdenum-blue method since the limit of detection is around 10 ppb [5].

In this task, the research group of Sabina Susmel and the postdoc student Federico Figueredo are working for the development of an orthophosphate electrochemical sensors for seawater and wastewater samples. The aim of our study is to develop a low cost, easy to use and sensitive electrochemical orthophosphate sensor that can be used for in field detection. As other

electrochemical sensors, the focus of the research is in the development of a new working electrode comprising the previously described characteristics.

General objectives

- Develop an orthophosphate electrochemical sensor sensitive enough to be used for seawater samples
- Test different formulations for the development of plastic working electrodes taking into account parameters as cost, disposability and flexibility, among others.
- Use and test different molybdate ions as precursors used to modify a plastic electrode and detect phosphate.

5

Particular objectives

- Study the possibility to include in the working plastic electrode, different precursors of phosphomolybdate complex such as ammonium heptamolybdate (commercial compound), tetrabutyl ammonium hexamolybdate or tetrabutyl ammonium octamolybdate. Characterize electrodes modifications with molybdate ions by electroanalytical techniques such as cyclic voltammetry and square wave voltammetry
- Characterize electrodes modification with molybdate ions by surface electron microscopy (SEM) techniques.
- Study the analytical response of the modified electrodes towards orthophosphate prepared in seawater simulated samples.

Summary

1_Preparation of plastic electrodes

2_Preparation and characterization of plastic electrodes modified with: 2a_ Ammonium heptamolybdate

2b_ Tetrabutylammonium hexamolybdate 2c_ Tetrabutylammonium octamolibdate

PARTE 2: PREPARATION OF THE COMPOSITE ELECTRODES AND CHARACTERIZATION

D 4.3.2 & D 4.3.3

Within the first month, we started to study different formulations for plastic working electrode preparation. The plastic electrode is produced at the laboratory with polyvinyl chloride (PVC), bis(2-ethylhexyl) adipate (BEA), synthesized graphite and tetrahydrofuran (THF, as the solvent). The

procedure to obtain a bare plastic electrode involves a first step of powder mixture, then the BEA and the solvent is added and finally the colloidal suspension is being agitated for about 20 min. When the suspension is ready, it is placed in a baker remaining at 25 °C until the solvent is completely evaporated. At the end, a plastic material with low resistivity (less than 100 ohms/cm) is obtained. To prepare a standard electrode to be incorporated in a standard three electrodes electrochemical cell, we cut the plastic material obtained with a round shaped commercial cutter used to cut paper. The electrodes are placed in a flexible PET layer (50 µm thickness, also called pouch) by using a double sided commercial tape available everywhere (Figure 1).

- 1) Colloidal suspension preparation: Graphite (380 mg) + BEA (50 mg)
+ PVC (50 mg) + THF (10 mL)
- 2) Colloidal suspension casting and drying process
- 3) Plastic conductive material is obtained
- 4) Electrode is being cut and prepared for electrochemical analysis



Figure 1. Brief description scheme showing the preparation steps to obtain a bare plastic electrode

In order to include molybdate ions in the formulation of the bare plastic electrode, we started using the commercial compound called ammonium heptamolybdate. This is a water soluble compound that is commonly used for colorimetric detection of phosphate since the reaction between them produce a phosphomolybdate complex. Moreover, as the phosphomolybdate complex is electroactive, several studies showed that it can be detected with different types of electrodes (most of them based on carbon materials). The first approach toward the detection of orthophosphate started from the detection of the phosphomolybdate complex in solution using a bare plastic electrode. This experiment will show us if the plastic electrode can react with the redox phosphomolybdate complex formed in solution. To do this, we followed methodologies applied by other researchers that used bare carbon electrodes (Cinti et al., 2016). As can be seen in the Figure 2, electrochemical measurements were done with the bare plastic electrode fabricated in our lab in

blank solutions (sulphuric acid 1 M and NaCl 0.6 M), blank solution with 1 mM of heptamolybdate anion in the absence/presence of orthophosphate. When heptamolybdate is in the sample, in the absence of orthophosphate an oxidation peak appears at around 1 V. However, when orthophosphate is present, the oxidation peak around 1 V increase, and also appear new oxidation peaks from 0.1 to 0.7 V. Reduction peaks appears only in presence of orthophosphate around 0.4 V. These behavior is similar to those reported by other authors but the problem remaining here is that the peaks are not well formed as it happened with other bare electrodes. This could be related to the surface characteristics of the plastic electrodes (Marsillia and Susmel, 2018).

In the following parts of this report we will summarize the methodology and the results obtained for the incorporation of different molybdate ions inside the plastic electrode formulation in order to increase the sensitivity and the characteristics of the electrode towards the detection and quantification of orthophosphate in seawater simulated samples.

7

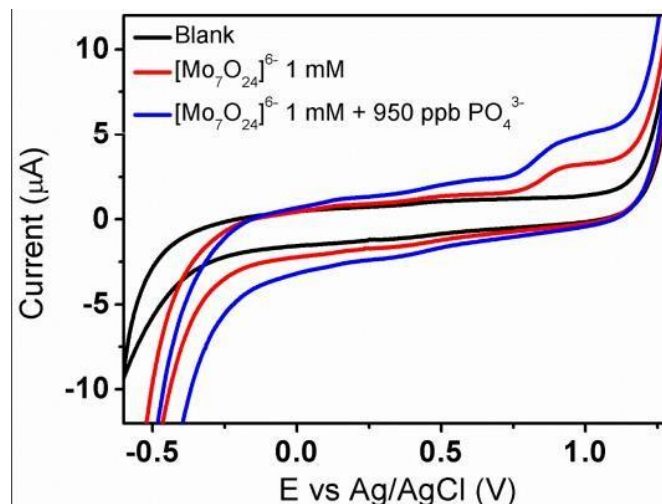


Figure 2. Cyclic voltammograms (25 mV/s) performed with bare plastic electrode after 60 min of incubation. Blank solution contain H₂SO₄ 1M and NaCl 0.6 M (35 g/L)

2a_Preparation and characterization of plastic electrodes modified with ammoniumheptamolybdate

To prepare a plastic electrode with heptamolybdate anions inside, we used the methodology described by Susmel group (Marsillia and Susmel, 2018) as was described previously in this report. The heptamolybdate was added as a powder (10, 20 and 40 mg) and the electrodes were prepared as usual. SEM analysis was done in order to identify the shape and distribution of molybdate anions over the electrode surface.

As can be seen in the Figure 3, the distribution of the heptamolybdate anions over the electrode surface is not homogeny. The presence of small and big crystals show that the compound was not dissolved in the solvent. This is possible because this compound is soluble in aqueous solvents.

To study the signal obtained with the modified eletrodes, cyclic voltammetry analysis was performed in solutions containing sulphuric acid 1M, NaCl 0.6M and different concentrations of

orthophosphate. In Figure 4 is possible to appreciate that the electrode responds to increasing concentrations of orthophosphate. Moreover the shape of the curve is similar to those obtained when heptamolybdate anions were in solution. In contrast, when heptamolybdate anions are included inside the electrode, the sensitivity of the electrode increase showing the possibility to use them for seawater samples analysis. However, the reproducibility obtained was very poor since the distribution of the heptamolybdate anions over the electrode surface was not good (RSD% greater than 25%). Results obtained with the electrodes prepared with different amounts of heptamolybdate anion showed similar results in terms of distribution over the electrode, reproducibility and intensity of the signals. Here as an example we show only the results obtained with electrode prepared with 10 mg of heptamolybdate anions.

An interesting fact is that the kinetic of the reaction between heptamolybdate anions included at the electrode and orthophosphate in solution is similar to those kinetic values that were reported for other assays made in solution, as can be seen in Figure 5.

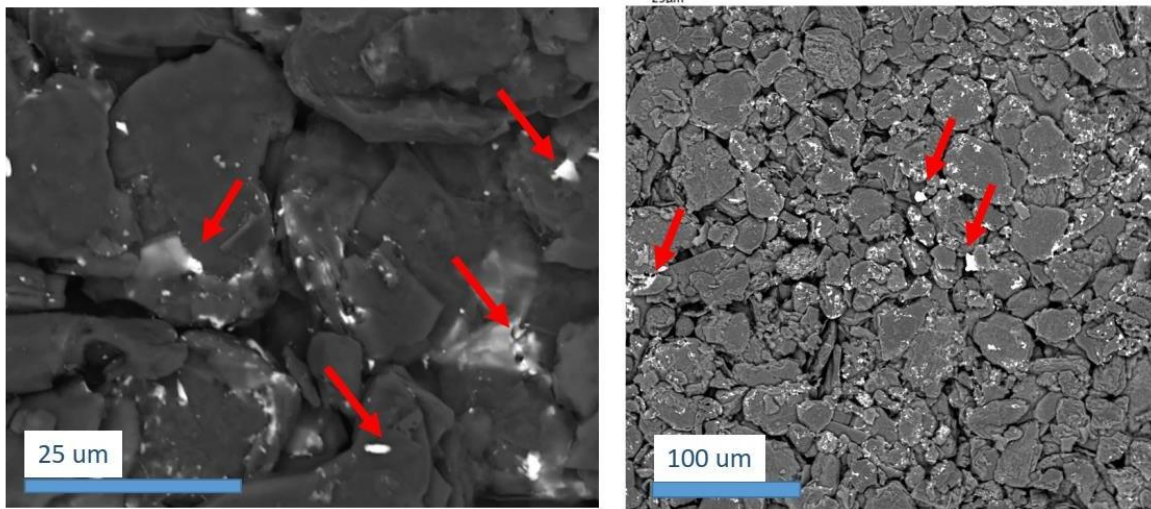


Figure 3. SEM pictures taken from the plastic electrode containing ammonium heptamolybdate (10 mg). Arrows indicate the localization of big ammonium heptamolybdate crystals and the distribution of them at different magnification

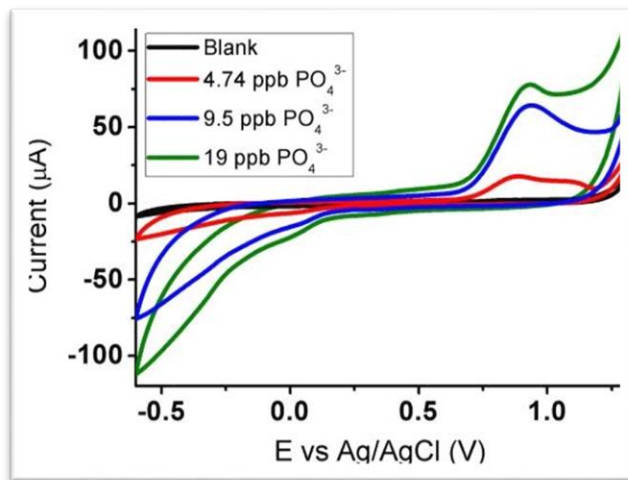


Figure 4. Cyclic voltammograms (25 mV/s) performed with plastic electrode prepared with 10 mg of $[\text{Mo}_7\text{O}_{24}]^{6-}$ (heptamolybdate) after 60 min of incubation. Blank solution contain H_2SO_4 1M and NaCl 0.6 M (35 g/L)

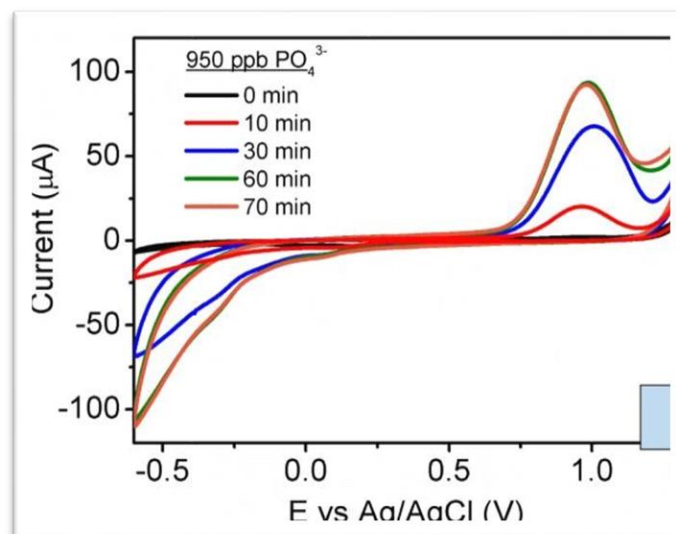


Figure 5. Cyclic voltammograms (25 mV/s) performed with plastic electrode prepared with 10 mg of $[\text{Mo}_7\text{O}_{24}]^{6-}$ (heptamolybdate). Measurements were done in a solution containing H_2SO_4 1M, NaCl 0.6M (35 g/L) and 950 ppb of PO_4^{3-} .

2b_Preparation and characterization of plastic electrodes modified with tetrabutyl ammonium hexamolybdate

Tetrabutyl ammonium hexamolybdate is typically obtained from molybdate oxides. We wanted to synthesize this compound since it can solubilized in non-aqueous solvents such as acetone and

dimethyl sulphoxide. However, there is not too much information about this compound and therefore we decided to try if we can solubilize it in other organic solvents as THF. The advantage is clear, if the hexamolybdate can be dissolved in THF (the solvent used to prepare the plastic electrode) we will probably obtain good distribution of the molybdate anions over the electrode surface.

The synthesis procedure was based on the protocol published by Hur and Klemperer (1990) in *Inorganic Syntheses*, Volume 27. Briefly, 1 g of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ was dissolved in 2 mL of distilled water. Then, 1 mL of HCl 6M was added when it was stirring in a 10 mL baker. After 10 min, 2 mL of a solution containing 0.78 g of tetrabutyl ammonium bromide was added and a white precipitate was obtained. The solution was heated at 70°C for 40 min and the precipitate was collected in a porosity filter with suction and washed with 60 mL of distilled water. The air-dried product was then dissolved in 40 mL of hot acetone and cooled at -20°C . After 24 hs a yellow crystalline powder was obtained.

The hexamolybdate prepared was dissolved in THF but the solubility was very low and when we prepared the plastic electrode the final amount of this compound was 4 mg. From the cyclic voltammetry analysis we saw the presence of hexamolybdate anions over the electrode since a high reduction peak was obtained as can be seen in the Figure 6. When the electrode is in contact with the solution that contains orthophosphate, the reduction signal decrease and no other signals appears. This behavior was obtained for several electrodes tested which indicates that probably the hexamolybdate reacts with orthophosphate (we tested from ppb to ppm concentrations) but the product is not an electroactive compound.

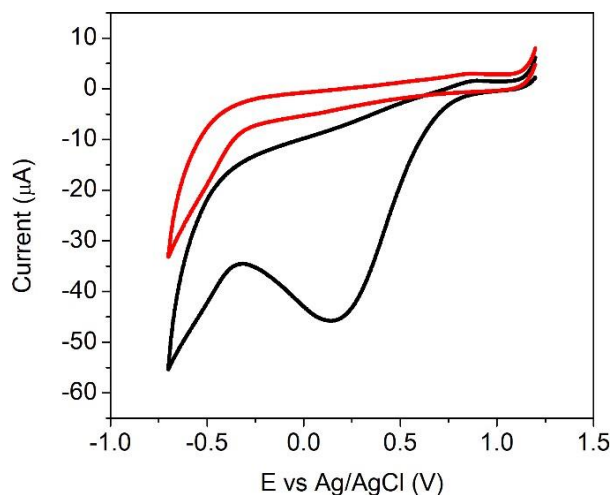


Figure 6. Cyclic voltammograms (25 mV/s) performed with plastic electrode prepared with 4 mg of tetrabutyl ammonium hexamolybdate. Measurements were done in a solution containing H_2SO_4 1M, NaCl 0.6 M (35 g/L) and 1 ppm of PO_4^{3-} .

Based on the results obtained after performing the cyclic voltammetry analysis with plastic electrodes modified with hexamolybdate, we decided to test another molybdate derivative called tetrabutyl ammonium octamolybdate.

2c_Preparation and characterization of plastic electrodes modified with with tetrabutyl ammonium octamolybdate

Tetrabutyl ammonium octamolybdate is another molybdate derivative that can be synthesized at the laboratory starting from a commercial salt of molybdate. The synthesis procedure was based on the protocol published by Hur and Klemperer (1990) in *Inorganic Syntheses*, Volume 27. Briefly, 1 g of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ was dissolved in 2 mL of distilled water. Then, 1 mL of HCl 6M was added when it was stirring in a 10 mL beaker. After 10 min, 2 mL of a solution containing 0.78 g of tetrabutyl ammonium

bromide was added and a white precipitate was obtained. The solution was collected in a porosity filter with suction and washed with 20 mL of distilled water, 20 mL of ethanol, 20 mL of acetone and 20 mL of diethyl ether. The air-dried product was then dissolved in 40 mL of acetonitrile and cooled at -20°C . After 24 hs a colorless crystalline powder was obtained.

To prepare the plastic electrode containing the octamolybdate, first the compound was dissolved in acetonitrile (100 g/L) or in propylene carbonate (100 g/L). Then, 200 μL of the stock solution (from acetonitrile or propylene carbonate) was added to 10 mL of THF. The plastic electrode was prepared in a similar way as before but using the THF containing the octamolybdate dissolved. The following part will show the results obtained for electrodes prepared when octamolybdate was added from acetonitrile or propylene carbonate stock solutions.

2b a Electrodes prepared from stock solutions of octamolybdate dissolved in acetonitrile

The first experiments were done using cyclic voltammetry techniques to identify the peak signals related to the octamolybdate included in the plastic electrode. To do this we measured in solutions containing different concentrations of sulphuric acid (0.1 M, 1 M and 5 M), NaCl 0.6 M and orthophosphate 1 μM (100 ppb). As can be seen in Figure 7, the concentration of sulphuric acid is important since the reactivity of octamolybdate towards orthophosphate increases. When sulphuric acid concentration of 5 M was employed, three oxidation peaks and two reduction peaks appear. However when concentration of sulphuric acid of 1 M or 0.1 M were employed, one oxidation peak and no peaks appear, respectively. Later, the effect of other acids as HCl was evaluated but in contrast with sulphuric acid, at higher concentrations (5 M) no defined peaks were obtained (Figure 8).

In order to explore the sensitivity of the electrode, we decided to employ sulphuric acid 5 M and prepare solutions with different amounts of orthophosphate. As can be seen in Figure 9, when the orthophosphate concentration increases, reduction and oxidation peaks increase too. In particular, we obtained a good response for the reduction peaks obtained at around 0 V. In Figure 10 it is possible to see the results of the analysis of this peak for three electrodes in the range of orthophosphate concentration studied.

In Figure 11 it is possible to appreciate the well distributed film containing octamolybdate anion. As can be seen, there is a great difference from those electrodes prepared with heptamolybdate. The good distribution of octamolybdate over the surface is a consequence of using a molybdate compound that can be dissolved in non-aqueous solvent.

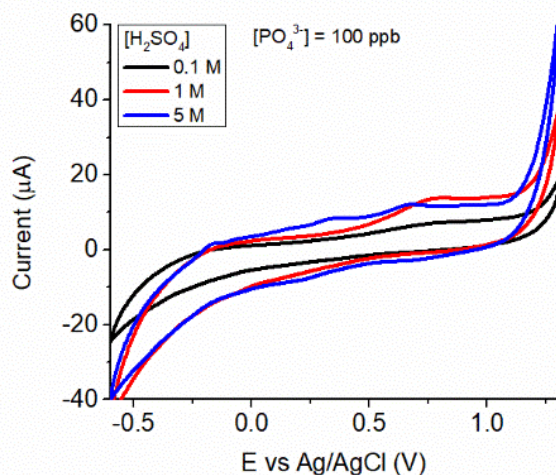


Figure 7. Cyclic voltammograms (50 mV/s) performed with plastic electrode prepared with 20 mg of tetrabutyl ammonium octamolybdate (from acetonitrile stock solution). Measurements were done in a solution containing H₂SO₄ 0.1 M (black lines), 1 M (red lines) or 5 M (blue lines). All solution contained NaCl 0.6 M (35 g/L) and 100 ppb of PO₄³⁻

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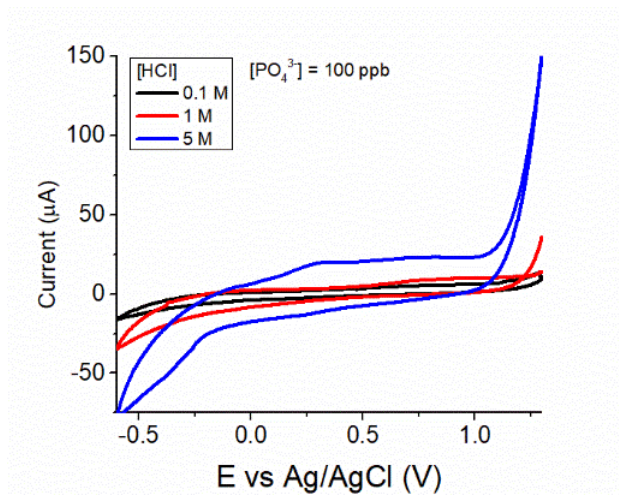


Figure 8. Cyclic voltammograms (50 mV/s) performed with plastic electrode prepared with 20 mg of tetrabutyl ammonium octamolybdate (from acetonitrile stock solution). Measurements were done in a solution containing HCl 0.1 M (black lines), 1 M (red lines) or 5 M (blue lines). All solution contained NaCl 0.6 M (35 g/L) and 100 ppb of PO₄³⁻

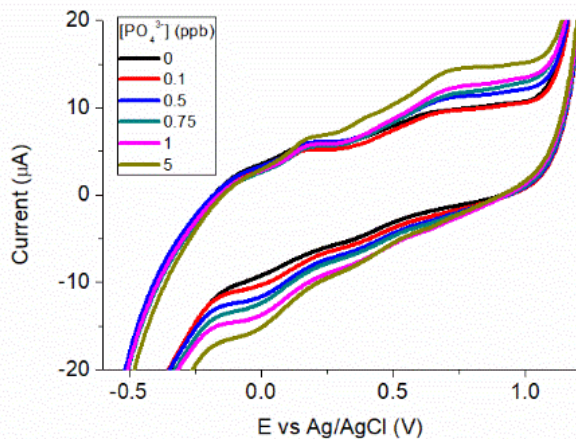


Figure 9. Cyclic voltammograms (50 mV/s) performed with plastic electrode prepared with 20 mg of tetrabutyl ammonium octamolybdate (from acetonitrile stock solution). Measurements were done in solution containing sulphuric acid 5M, NaCl 0.6 M (35 g/L) and different concentrations of PO_4^{3-} . 4

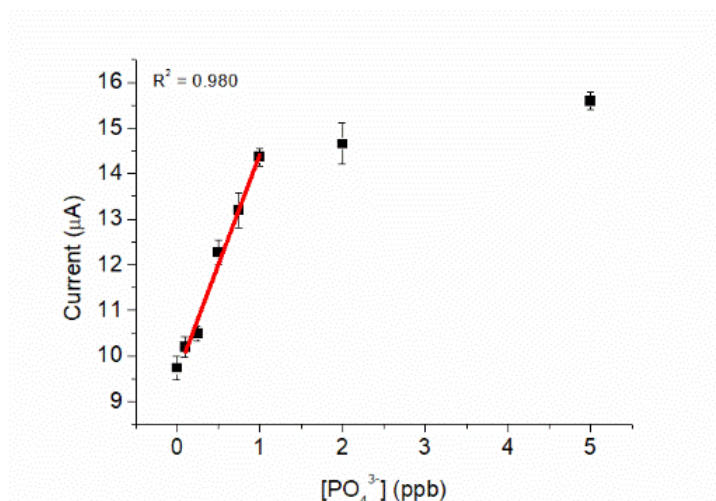


Figure 10. Calibration curve obtained from cyclic voltammograms performed with plastic electrode prepared with 20 mg of tetrabutyl ammonium octamolybdate (from acetonitrile stock solution) in sulphuric acid 5M, NaCl 0.6 M (35 g/L) and different concentrations of PO_4^{3-} . The current obtained is from a reduction peak at 0 V ($n = 3$).

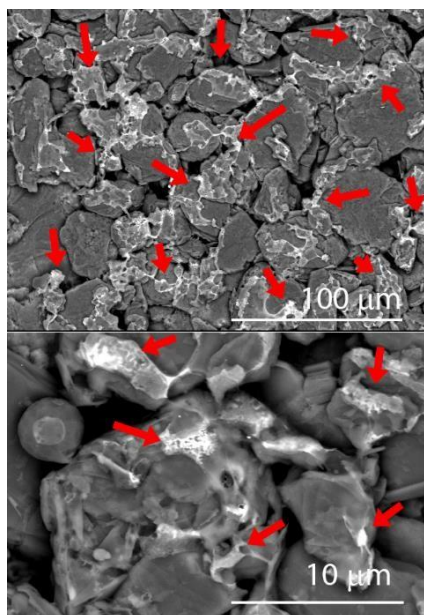


Figure 11. SEM pictures taken from the plastic electrode containing tetrabutyl ammonium octamolybdate (20 mg). Arrows indicate the localization of octamolybdate films and the distribution of them at different magnification.

2 b c Electrodes prepared from stock solutions of octamolybdate dissolved in propylene carbonate

The plastic electrode containing octamolybdate was prepared as the same way than before but the only thing that was changed was the solvent used to prepare the stock solution of octamolybdate. We decided to use propylene carbonate since that previous experiment showed us the marked differences between acetonitrile and propylene carbonate when octamolybdate was analyzed in solution by using cyclic voltammetry analysis and bare glassy carbon electrodes (data not shown).

When the plastic electrode was constructed with octamolybdate previously dissolved in propylene carbonate the results were very different from those obtained when octamolybdate was dissolved in acetonitrile. First of all, the cyclic voltammetry now show 4 redox couples that are in agreement with previously reported results from carbon based electrodes modified with octamolybdate anions. Second, the reactivity of this electrode seems to be enhanced since we obtain well described peaks with lower acid concentrations (1 M) than those used before (5 M) as can be seen in Figure 12.

In Figure 13 is possible to see the result of a square wave voltammogram obtained with blank solutions without orthophosphate. After analyzing this curves we appreciated that the same four oxidation peaks that appear in the cyclic voltammetry appear in the square wave voltammetry and the first peak responds to orthophosphate increasing the current signal as can be seen in Figure 14.

Future work will be done with this type of electrode and several analysis will be planned for the next months. The possibility to use a plastic electrode containing octamolybdate previously prepared from propylene carbonate is an important advantage since the analysis of orthophosphate can be done in concentrations of sulphuric acid that are easy to use by trained personnel.

In the next 6 months, we will study and optimize the electrochemical sensor in order to reach the objectives planned in this project.

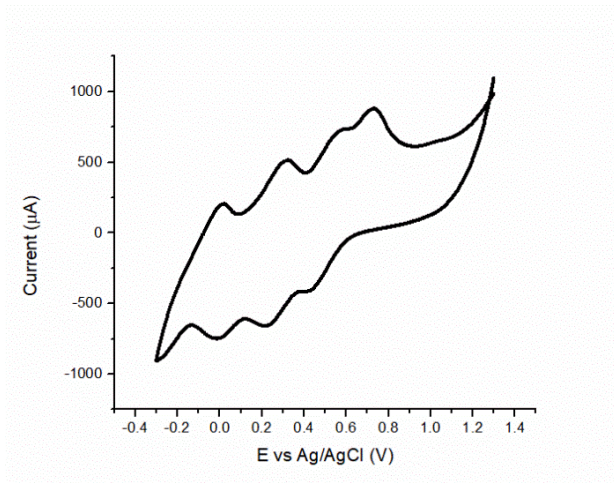


Figure 12. Cyclic voltammograms (50 mV/s) performed with plastic electrode prepared with 20 mg of tetrabutyl ammonium octamolybdate (from propylene carbonate stock solution). Measurements were done in a solution containing sulphuric acid 1M and NaCl 0.6 M (35 g/L).

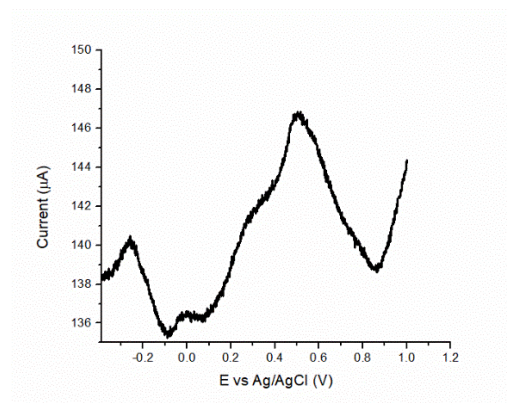


Figure 13. Square wave voltammograms (f 25 Hz) performed with plastic electrode prepared with 20mg of tetrabutyl ammonium octamolybdate (from propylene carbonate stock solution). Measurements were done in a solution containing sulphuric acid 1M and NaCl 0.6 M (35 g/L).

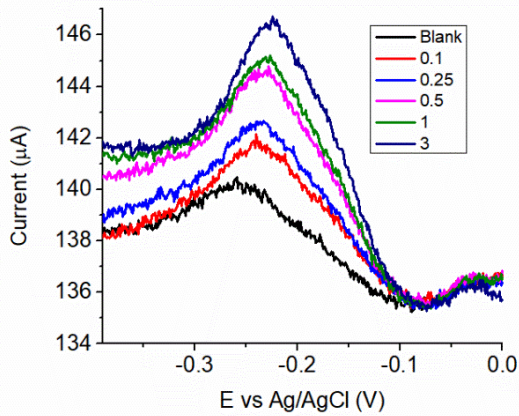


Figure 14. Square wave voltammograms (f 25 Hz) performed with plastic electrode prepared with 20mg of tetrabutyl ammonium octamolybdate (from propylene carbonate stock solution).

Measurements were done in a solution containing sulphuric acid 1M, NaCl 0.6 M (35 g/L) and different concentrations of PO_4^{3-} .

2 c electrodes prepared by addition of nanoparticles mesoporous silica-based and octamolybdate

The E-sensor was further optimised by adding to the plastic electrode periodic meso-porous organosilica nanoparticles (PMO) (Figure 5, B) that, we believed through a mechanism of preconcentration, locally enrich of MOP the electrode surface enhancing the sensitivity, measuring as new DL 1 nM of DIP (Figure 5, C). The characterization of this new formulation/electrode was performed by SEM and EDX analysis associated with the electrochemical investigation of standard samples. Then the E-sensor was applied to both wastewater samples and seawater coming from the sampling points above-mentioned (Figure 2, Table 2) with a recovery rate of 98% (paper in progress).

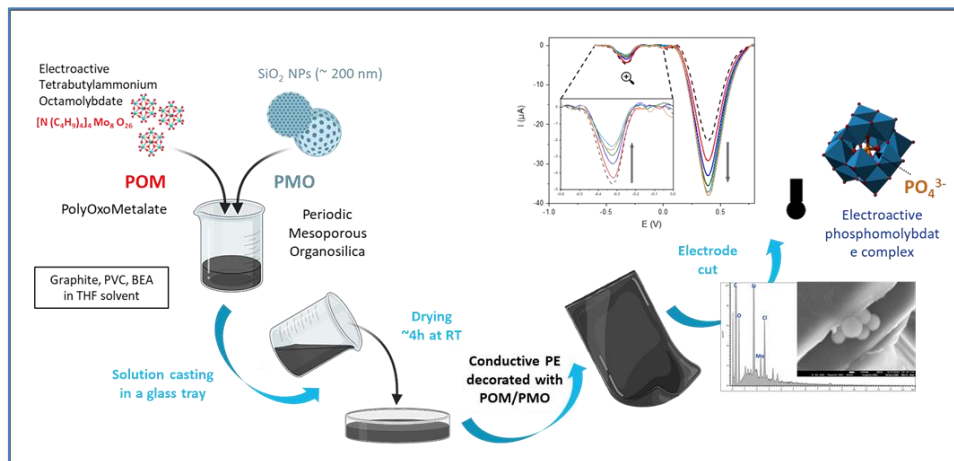


Figure 15: Scheme for the E-sensor preparation for phosphate detection in the two formulations adopted (A and B) and signal of enhanced sensitivity measured in presence of DIP (C).

PARTE 3: PERFORMANCES AND COMPARISON WITH OTHER ELECTRODES

D 4.3.4

The results obtained are now under critical analysis and revision and the preparation of the manuscript titled “POM@PMO Plastic Electrodes for Orthophosphate Electrochemical Detection: A Further Improvement of The Detection Limitis” is now in progress. The advantages offered by the electrode here further optimized can be summarized in a higher sensitivity if compared with both the previous invented by us and the existing devices/instrumentations. Moreover, it has been possible to measure in real samples without further actions of sample preparation apart dilution. Finally, contacts are open with WATERCARE project as well to implement, with their technical support, the E-sensor with the aim of adding it to a central unit analyzing wastewater treated discharged in recipient water (durability of the Adswim Interreg project).

Table 1. Analytical performances of some available sensors used to detect phosphate.

Electrode Composition	Method	Sample	Linear range	LOD	Reagents addition	Inc. time	Ref.
POM@PMO	SWV	Sea water waste water	1-100 nM	1 nM	H ₂ SO ₄	No	This study, further implement
Mo-PE 1	SWV	Sea water	1–75 nM	6.1 nM	H ₂ SO ₄	No	[8]
NHH on the NF surface	Amp	Waste water	0.010–14 mM	420 nM		6 s	[9]
Molybdenum modified GE	blue DPV	Soil	0.025–1 μM	20 nM	H ₂ SO ₄	60 min	[10]
Paper SPE/CB	CV	River water	10–300 μM	4 μM	Mo ₇ O ₂₄ ⁶⁻ , H ₂ SO ₄ and KCl (on paper)	No	[11]
Rotating gold electrode	disk Amp	Sea water	0.59–3.39 μM	110nM	No	1080 s	[12]
PSS/PEDOT/Chit/Mo ₇ O ₂₄ ⁶⁻ -GCE	Amp	No	0.19–95 μM	n.s.	Tris buffer	No	[13]

SPE: screen printed electrode; GE: graphite electrode; NHH: nanoflower-like Ni hydrated hydroxide; NF: nickel foil; CB: carbon black; PSS: polystyrenesulphonate; PEDOT: poly (3,4-ethylene dioxythiophene); Chit: chitosan; Amp: amperometry; DPV: differential pulse voltammetry.

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