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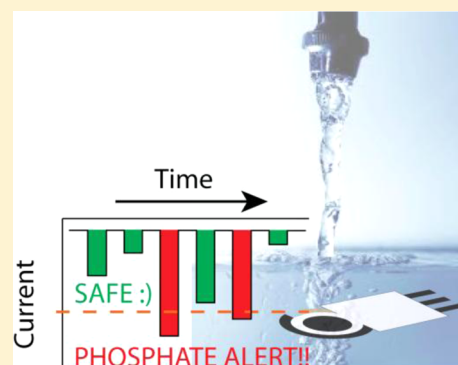
Phosphate Detection through a Cost-Effective Carbon Black Nanoparticle-Modified Screen-Printed Electrode Embedded in a Continuous Flow System

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ABSTRACT: An automatable flow system for the continuous and long-term monitoring of the phosphate level has been developed using an amperometric detection method based on the use of a miniaturized sensor. This method is based on the monitoring of an electroactive complex obtained by the reaction between phosphate and molybdate that is consequently reduced at the electrode surface. The use of a screen-printed electrode modified with carbon black nanoparticles (CBNPs) leads to the quantification of the complex at low potential, because CBNPs are capable of electrocatalytically enhancing the phosphomolybdate complex reduction at +125 mV versus Ag/AgCl without fouling problems. The developed system also incorporates reagents and waste storage and is connected to a portable potentiostat for rapid detection and quantification of phosphate. Main analytical parameters, such as working potential, reagent concentration, type of cell, and flow rate, were evaluated and optimized. This system was characterized by a low detection limit ($6 \mu\text{M}$). Interference studies were carried out. Good recovery percentages comprised between 89 and 131.5% were achieved in different water sources, highlighting its suitability for field measurements.



1. INTRODUCTION

Essential biomolecules, such as nucleic acids and phospholipids, and almost all metabolic reactions, including photosynthesis, respiration, and energy delivery, need one of the most vital elements for all living organisms, which acts as a constituent: phosphorus (P). Nevertheless, this key element needs to be regulated and monitored to avoid an excessive concentration capable of promoting eutrophication, which is well-known as the most widespread water-quality problem.¹ It causes harmful increased biomass of phytoplankton and macrophyte vegetation; it shifts to bloom-forming algal species that might be toxic; and it increases the incidence of fish kills and the reduction in species diversity.^{2,3} Scientists agree that it is largely caused by increasing inputs of phosphorus and nitrogen, which are abundant in human sewage, in the excrement of livestock, and in synthetic fertilizers applied to agricultural land.⁴ However, the problem of eutrophication is to be sought as a primary cause in humans; in fact, the industrial development is also leading to phosphorus pollution. In addition, agricultural fertilizers are obtained using 80% of all of the mined phosphorus rock. The remaining is used in animal feed, beverages, toothpastes, and industrial applications, such as detergents, electrical sensors, and semiconductors.^{5,6} Phosphate in natural water largely consists of orthophosphate up to 0.01 ppm;⁷ also, some organic forms are present (detergents) but

are gradually hydrolyzed to orthophosphate. The phosphate level in water is regulated by the European Union (EU) through the Urban Waste Water Treatment Directive (annual mean total phosphorus concentrations of 1–2 mg/L) and the Water Framework Directive that will enforce “good ecological and chemical status” by 2015.⁸ The need, besides a reasonable use of the source materials containing high amounts of phosphate, concerns their monitoring in the sea, rivers, and lakes as well as in the wastewater samples of industrial factories. The analytical field should provide detection methods that are easy-to-use, long-lasting, and cost-effective about their manufacture and maintenance. The standard method for measuring soluble phosphate in water is a colorimetric technique developed by Murphy and Riley⁹ based on the formation of a blue-colored complex between phosphate and molybdate ions; to this regard, several methods have been developed for the determination of phosphate in various matrices using different techniques, including chromatography, ultraviolet–visible (UV–vis), fluorescence, and electroanalysis.^{10–13}

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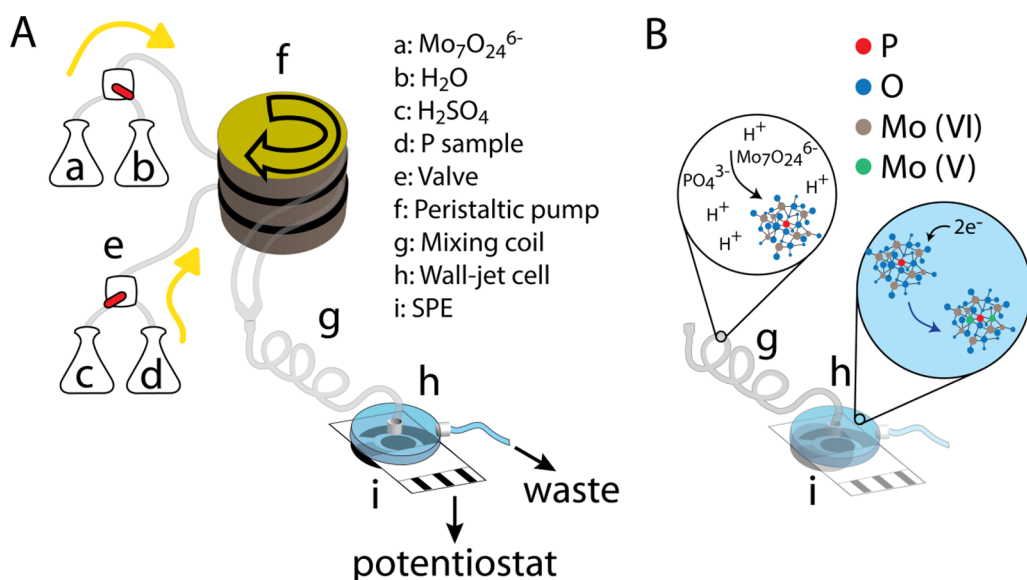


Figure 1. (A) Schematic representation of the apparatus for continuous flow for phosphate analysis. (B) Reaction involved in the formation of the phosphomolybdate complex and its reduction at the working electrode surface.

In the literature, many works have been reported for the continuous determination of phosphate. Systems based on spectrophotometric detection were among the first analytical devices developed, because they are based on the reference method.^{14,15} These colorimetric approaches are usually based on the phosphomolybdate blue complex and characterized by the turbidity.¹⁶ These methods are affected by silicate interference; the silicomolybdate blue complex has a broad absorbance band (790 nm) that overlaps 710 nm typically used for phosphomolybdate blue detection.¹⁶ Rohwedder's group¹⁷ reported a monosegmented flow system for the determination of phosphate in water, by employing the reaction between molybdophosphate and malachite green, characterized by high absorption at 650 nm. Nevertheless, the colorimetric setup could be difficult to adapt for online measurements, because it requires a lot of reagents and one of them is unstable (ascorbic acid).

The advantage of electroanalytical techniques lies in the fact of not requiring ascorbic acid because the reduction occurs at the electrode surface. Furthermore, they are characterized by cost-effective equipment and suitable to be used directly *in situ* by means of portable equipment interfaced with a laptop. Monitoring of phosphate, particularly at a level of industrial factories, is appealing, and then the requirement of methods that are disposable and robust at the same time acquires more importance. Udnan et al.¹⁸ reported a flow injection analysis (FIA) amperometric method based on a glassy carbon electrode (GCE) to detect dissolved phosphate in fresh and marine waters based on reduction of the product formed from the reaction of phosphate with molybdate in acidic media. In this work, we propose a disposable sensor based on a screen-printed electrode modified with carbon black nanoparticles (CBNPs) embedded in a continuous flow system. The electrocatalytic properties of this cost-effective nanomaterial was recently demonstrated by our research group toward several analytes, such as hydrogen peroxide, reduced nicotinamide adenine dinucleotide (NADH), thiocholine, and cysteine,^{19–22} and then extensively studied by other groups.^{23–26} Herein, we successfully extend the employment of CNBP-modified screen-printed electrode (SPE), previously

optimized for batch measurements by our group,²⁷ for the realization of an automatic continuous flow system capable of detecting phosphate in water, by measuring the electroactive phosphomolybdate complex. This complex is easily revealed by this electrochemical platform using a low applied potential and avoiding interferences, i.e., silicate, arsenate, and nitrate, showing a satisfactory repeatability, robustness, and resistance to fouling.

2. EXPERIMENTAL SECTION

2.1. Apparatus and Reagents. Sulfuric acid (95–98%), ammonium heptamolybdate tetrahydrate, potassium chloride, potassium dihydrogen phosphate, potassium nitrate, 1000 ppm of Cu(II) atomic absorption spectroscopy (AAS) standard solution, and 1000 ppm As(V) inductively coupled plasma mass spectrometry (ICP–MS) standard solution were purchased from Sigma-Aldrich (St. Louis, MO), and 1000 ppm of As(III) ICP–MS standard solution was purchased from Inorganic Ventures (Christiansburg, VA). Continuous flow amperometric measurements were performed using a portable PalmSens Instrument (PalmSens, Netherlands) in connection with a personal computer. UV–vis measurements were obtained using a spectrophotometer UV 1800 (Shimadzu, Japan).

2.2. SPE Fabrication. SPEs were produced with a 245 DEK (Weymouth, U.K.) screen-printing machine. Conductive inks were purchased from Acheson (Italy): carbon ink (Electrodag 421) was used to print working and counter electrodes, while Ag/AgCl ink (Electrodag 477 SS) was used to print the pseudo-reference electrode. The substrate was a flexible polyester film (Autostat HTS) obtained from Autotype Italia (Italy). The diameter of the working electrode was 0.3 cm.

2.3. CNBP Dispersion. The dispersion of carbon black nanoparticles (CBNPs) was prepared by adding 10 mg of CB N220 powder to 10 mL of a 1:1 mixture of dimethylformamide and water, then the dispersion was sonicated for 60 min at 59 kHz.

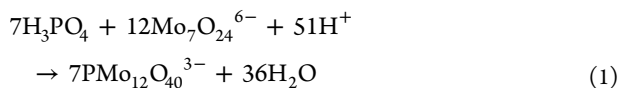
2.4. Preparation of CNBP–SPE. A total of 6 μ L of CNBP dispersion was cast onto a SPE working electrode surface in three steps of 2 μ L each. The solvent was allowed to volatilize,

forming a CBNP film, and these sensors were stable for at least 100 days at room temperature.

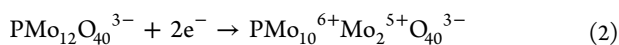
2.5. Phosphate Detection. The automatable flow detection system is reported in Figure 1A. Reagents, i.e., ammonium eptamolybdate, water, sulfuric acid, and phosphate sample, were stored in four different containers, a, b, c, and d, respectively. The valves (e) were capable of selectively aspirating a or b and c or d solutions. A multi-channel peristaltic pump (Gilson model M312, France) (f) drew up the reagents at a flow rate equal to 0.5 mL min^{-1} through Tygon tubes characterized by an internal diameter of 0.51 mm. Reagents were pumped into a 30 cm long mixing coil (g) to allow for the desirable reaction to produce the electroactive complex (Figure 1B) that flowed in a wall-jet cell (h) and was quickly detected because it was reduced at CBNP–SPE (i) connected to a potentiostat (PalmSens). Reagent solutions were wasted as illustrated. The flow cell was homemade and specially adapted for this particular SPE configuration. This modified cell allowed for an easy and reproducible replacement of the SPE. An O-ring located at the cover helped to close tightly the electrochemical cell, confining the flow cell volume.

3. RESULTS AND DISCUSSION

Recently,²⁷ we demonstrated the electrochemical properties of CBNPs toward the electroactive phosphomolybdate, also known as Keggin anion, as a product deriving from the reaction of phosphate ions in the presence of molybdate in strong acidic media,²⁸ as reported in eq 1.



This complex was easily reduced to a mixed molybdenum oxidation state and detected at low potential by amperometry, as displayed in the following equation (eq 2):



Cyclic voltammetry studies reported in our previous work showed two redox pairs relating the phosphomolybdate complex around +100 and +200 mV, respectively (versus Ag/AgCl). We observed an excellent enhancement of the electrochemical response by modifying SPE with CBNPs; sensitivity to phosphate increased 20-fold using CBNP–SPE instead of bare SPE.²⁷

However, the development of a flow system requires satisfactory sensitivity, repeatability, and especially response time that should not be excessively long; also, avoiding the use of excessive amounts of sample will help to reduce the waste. We first studied the optimization of the applied potential and the concentration of sulfuric acid to obtain the electroactive complex in a high yield. The concentration of molybdate was 1 mM, as reported in the previous work.²⁷ Figure 2A shows the sensitivity reached by applying different potentials to reduce the phosphomolybdate complex, and despite the maximum sensitivity achieved working with +100 mV, the potential used was +125 mV; a better compromise between sensitivity and repeatability (calculated as the relative standard deviation on three replicates, RSD on $n = 3$) was found equal to 9.2 and 2.5% at 100 and 125 mV, respectively. From observation of eq 1, it is easy to figure out how the concentration of H^+ ions plays a fundamental role in the formation of the complex, which occurs only at extremely acidic pH. It is important to define an

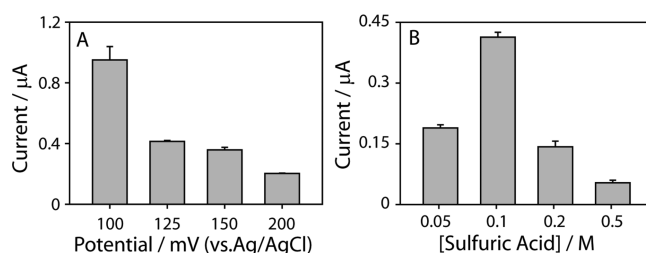


Figure 2. (A) Optimization of the working potential in the range between 100 and 200 mV (versus Ag/AgCl). Experimental parameters: $[\text{Mo}] = 1 \text{ mM}$, $[\text{PO}_4^{3-}] = 50 \text{ μM}$, $[\text{H}_2\text{SO}_4] = 0.1 \text{ M}$, $[\text{KCl}] = 0.1 \text{ M}$, flow rate = 0.5 mL min^{-1} . (B) Optimization of the concentration of sulfuric acid in the range comprised between 0.05 and 0.5 M. $[\text{Mo}]$, $[\text{PO}_4^{3-}]$, $[\text{KCl}]$, and flow rate were chosen similar to those used for the working potential optimization. A potential of +125 mV (versus Ag/AgCl) was applied.

exact relationship between the concentration of H^+ and Mo, so that the kinetic of the complex formation is favored, especially for a flow system in which the response must be fast. The optimum concentration of sulfuric acid was found to be 0.1 M, as shown in Figure 2B, which provided the best sensitivity and a satisfactory RSD equal to 2.9%. The optimal ratio H^+/Mo turned out to be equal to 100, in which results were comparable to that used in the work by Jońca et al.,²⁹ in which a ratio of 70 was chosen.

Because this is a flow system, length and diameter of the tubing were also optimized to allow for a better reaction, especially along the mixing coil, and the highest sensitivity was obtained for a 30 cm long mixing coil with an internal diameter of 0.51 mm.

Considerable importance also concerns the way in which the sample comes in contact with the sensitive area of the sensor; the cell, where the sensor is positioned, requires considerable care in its design. Two cell kinds were evaluated, a wall jet and a thin layer. From the histograms displayed in Figure 3A, even if

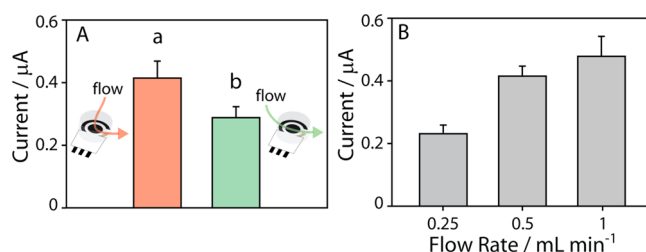


Figure 3. (A) Choice of the flow cell configuration: (a) wall jet and (b) thin layer. Experimental parameters: $[\text{Mo}] = 1 \text{ mM}$, $[\text{PO}_4^{3-}] = 50 \text{ μM}$, $[\text{H}_2\text{SO}_4] = 0.1 \text{ M}$, $[\text{KCl}] = 0.1 \text{ M}$, flow rate = 0.5 mL min^{-1} , $E_{\text{app}} = +125 \text{ mV}$ (versus Ag/AgCl). (B) Optimization of the flow rate between 0.25 and 1 mL min^{-1} , with the same experimental conditions used for the choice of the flow cell.

the repeatability is comparable (RSD = 14% for the wall-jet cell, and RSD = 12% for the thin-layer cell), it is clear that the use of the wall-jet cell led to a better sensitivity compared to that obtained using the thin-layer cell. This is due to the fact that the solution, flowing from the inlet capillary, hits perpendicularly on the working electrode and the flow takes place radially in three dimensions. The wall-jet electrode has been largely studied, both theoretically and experimentally; it is an interesting configuration considering its high convective mass-transfer characteristics.³⁰ Because of the jet flow, two main

advantages are achieved: the response is fast, and the electrode area is mechanically cleaned, reducing the problems related to fouling. Another parameter optimized was the flow rate, which contributes greatly to the sensitivity of a flow procedure. Following the choice of the type of measuring cell, the best results were obtained using a flow rate of 0.5 mL min^{-1} , consistent with a RSD of 2%. Further, doubling the rate up to 1 mL min^{-1} , we did not observe a doubling of sensitivity, as displayed in Figure 3B.

The analytical features of the CBNP-modified electrode were evaluated using standard solutions of phosphate. Under the optimized conditions, the flow system showed a linearity up to $80 \text{ }\mu\text{M}$ phosphate, described by the regression equation $y = 7.02x - 29.6$, where y is the current (nA) and x is the phosphate concentration (μM), with a very satisfactory correlation coefficient $R^2 = 0.995$, as illustrated in Figure 4.

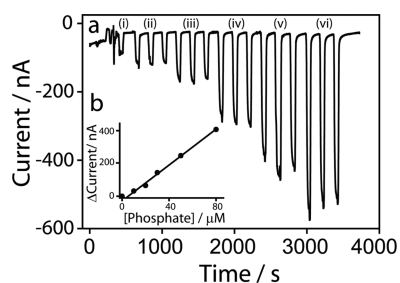


Figure 4. (a) Flow amperometric signals recorded for detection of (i) 0, (ii) 10, (iii) 20, (iv) 30, (v) 50, and (vi) $80 \text{ }\mu\text{M}$ phosphate. (b) Calibration curve obtained by the current signals recorded from the flow analysis ($n = 3$) subtracted from the value of the molybdate background signal. Experimental parameters: $[\text{Mo}] = 1 \text{ mM}$, $[\text{H}_2\text{SO}_4] = 0.1 \text{ M}$, $[\text{KCl}] = 0.1 \text{ M}$, flow rate = 0.5 mL min^{-1} , and $E_{\text{app}} = +125 \text{ mV}$ (versus Ag/AgCl).

The detection limit (LOD), calculated as $3\sigma_b/\text{slope}$, was found to be $6 \text{ }\mu\text{M}$, and the repeatability (RSD) evaluated at $50 \text{ }\mu\text{M}$ phosphate was 4% ($n = 3$). The analytical performances of the developed sensor are competitive with performances obtained using the phosphate-sensor based on the precipitation of molybdophosphate on GCE reported recently by Zheng et al.³¹ Indeed, this sensor is characterized by a linear range up to 100 ppm (1.05 mM), LOD of 10 ppm ($105 \text{ }\mu\text{M}$), and sensitivity equal to $4 \text{ }\mu\text{A}/\text{mM}$.

The relevance of the developed analytical method was characterized by its degree of agreement among the various measurements; repeatability was tested by comparing the responses for 20 consecutive measurements of phosphate at $50 \text{ }\mu\text{M}$ using the same sensor (Figure 5). The relative standard deviation was equal to 9.3%, demonstrating the good repeatability of this analytical tool because of the good electrochemical properties of CBNP-SPE.

One of interferences affecting the determination of phosphate during the phosphomolybdate complex formation is represented by silicate. As widely reported in the literature, silicate can form a complex with molybdate and interferes in the measurement of phosphate.³² In a previous work,²⁷ the non-interference related to silicate in this experimental condition has been convincingly demonstrated. In this work, we evaluated the selectivity of this method in the presence of other interfering species, such as As(III) ($6.7 \text{ }\mu\text{M}$), As(V) ($6.7 \text{ }\mu\text{M}$), Cu^{2+} ($1.6 \text{ }\mu\text{M}$), and NO_3^- ($3.2 \text{ }\mu\text{M}$). As seen in Figure 6, these ions did not exhibit a significant interference when

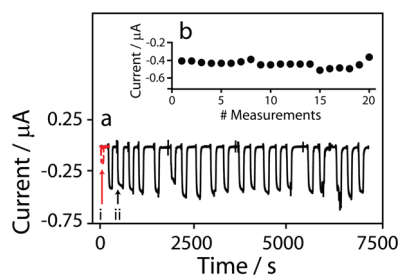


Figure 5. (a) Flow amperometric signals acquired by measuring (i) solution without phosphate and (ii) solution containing $50 \text{ }\mu\text{M}$ phosphate ($n = 20$). (b) Current values related to 20 sequential measurements of $50 \text{ }\mu\text{M}$ phosphate solution. Experimental parameters as in the caption of Figure 4.

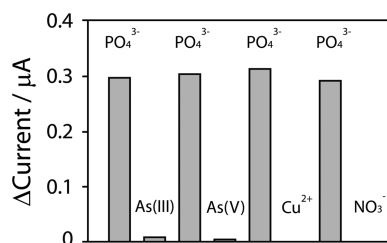


Figure 6. Interference studies in the presence of $50 \text{ }\mu\text{M}$ phosphate + $6.7 \text{ }\mu\text{M}$ As(III), $6.7 \text{ }\mu\text{M}$ As(V), $1.6 \text{ }\mu\text{M}$ Cu^{2+} , and $3.2 \text{ }\mu\text{M}$ NO_3^- , with experimental parameters as in the caption of Figure 4.

present; indeed, the signal recorded in their presence was of the same magnitude as the signal recorded for only molybdate in the absence of phosphates (background signal), demonstrating the absence of the interference of these compounds at the level tested ($0.1\text{--}0.5 \text{ ppm}$).

Recovery experiments were also performed; three different sources, tap water (collected at our laboratory), river water (Tiber river, Rome, Italy), and lake water (Albano, Rome, Italy), were spiked with known amounts of phosphate ($20 \text{ }\mu\text{M}$), and the percentage recoveries were analyzed by the electrochemical continuous flow system and the reference spectrophotometric assay, displayed in Table 1. The recovery values

Table 1. Percentage Recoveries of $20 \text{ }\mu\text{M}$ Phosphate in Different Media Comparing the Electrochemical Results to the Spectrophotometric Reference Method ($n = 3$)

water sample spiked with $20 \text{ }\mu\text{M}$	electrochemical method		spectrophotometric method	
	phosphate found (μM) $\pm \sigma$	recovery (%) $\pm \sigma$	phosphate found (μM) $\pm \sigma$	recovery (%) $\pm \sigma$
Tor Vergata laboratory (Rome, Italy)	25.4 ± 1.6	127 ± 8	25.0 ± 0.1	125.0 ± 0.5
Tiber river (Rome, Italy)	18.4 ± 2.0	92 ± 10	17.8 ± 0.2	89 ± 1
Albano lake (Rome, Italy)	20.8 ± 1.2	104 ± 6	26.3 ± 0.1	131.5 ± 0.5

obtained by the spectrophotometric method were characterized by higher accuracy when compared to those obtained by the electrochemical method. This behavior can be ascribed at the manually fabrication of the sensor with CBNPs, because each real sample was analyzed with three different sensors ($n = 3$); however, e.g., using an automatic Biodot dispensing equipment (www.biodot.com), we are confident that the good accuracy found with the electrochemical continuous flow system can be

further improved. Figure 7 displays an amperometric response related to a tap water sample spiked with 20 μM phosphate.

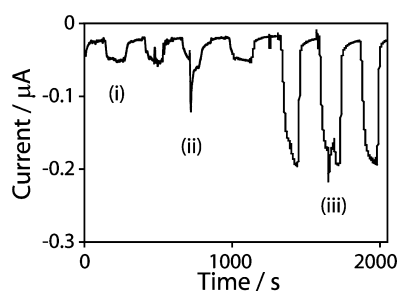


Figure 7. Flow amperometric signals acquired by measuring a (i) solution without phosphate, (ii) tap water sample, and (iii) tap water sample spiked with 20 μM phosphate, with experimental parameters as in the caption of Figure 4.

Even if the recorded current–time curve appears to be a little bit jagged, it is evident how (i) the sample spiked with 20 μM phosphate gave a higher signal than the unspiked real sample and (ii) three successive measurements were well-correlated to each other, demonstrating the suitability of the proposed analytical system for the detection of phosphate in real matrices.

Taking into account the good results obtained, this system could be used for online detection of phosphate in many domains, such as rivers, lakes, and also industrial wastewaters. Furthermore, the data can be further recorded via wireless smartphones (www.palmsens.com) with no need of personnel and expensive equipment.

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Author Contributions

*Daria Talarico and Stefano Cinti contributed equally to this work.

Notes

The authors declare no competing financial interest.

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