



# Novel reagentless paper-based screen-printed electrochemical sensor to detect phosphate



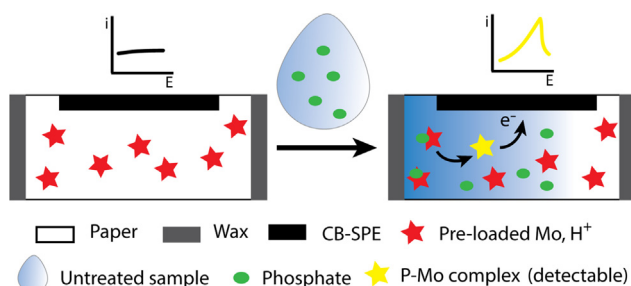
Stefano Cinti, Daria Talarico, Giuseppe Palleschi, Danila Moscone, Fabiana Arduini\*

Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma Tor Vergata, Via Della Ricerca Scientifica 1, 00133 Rome, Italy

## HIGHLIGHTS

- Devices were prepared coupling wax/screen-printing technologies.
- Facile, cost-effective, and rapid manufacturing route.
- Impregnated-paper stores all the necessary reagents.
- No sample treatment required to detect phosphate.
- Concept easy extensible to different analytes.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 9 September 2015  
 Received in revised form  
 29 February 2016  
 Accepted 7 March 2016  
 Available online 18 March 2016

### Keywords:

Paper-based electroanalytical platform  
 Wax-printing  
 Screen-printed electrodes  
 Reagentless  
 Phosphate  
 User-friendly method

## ABSTRACT

Herein we describe a novel reagentless paper-based electrochemical phosphate sensor, manufactured with a simple and inexpensive approach. By following three easy steps, consisting of wax patterning, paper chemical modification, and electrode screen-printing, the filter paper provides an effective electroanalytical platform to sense phosphate ions in standard solutions and real samples (river water). The electrochemical properties of the paper-based platform were evaluated, firstly, by using ferricyanide as a redox mediator, proving no analyte-entrapment due to the cellulose lattice. Then, the reference colorimetric method for phosphate ions, which is based on the formation of phosphomolybdic complex, was successfully adapted to a reagentless electrochemically paper-based platform. This novel and highly sustainable configuration readily allows for the determination of phosphate ions with high reproducibility and long storage stability, achieving a detection limit of 4  $\mu\text{M}$  over a wide linear range up to 300  $\mu\text{M}$ . This in-house approach would be able to generically develop an affordable *in situ* and user-friendly sensing device without the addition of any reagent, to be applied for a broad range of analytes.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

Nowadays, it is well known that a high concentration of essential elements, such as phosphorous (P) and nitrogen (N) in their anionic forms, can be harmful to the aquatic environment.

Eutrophication, better known as the excessive growth of aquatic plants and algae, involves a serious threat to aquatic species [1–3]. The increase of biomass, disruption of aquatic life cycles, fish death, and toxin production, represent some of the major consequences of this phenomenon [4]. Phosphorus ranges from 0.2 to 10 ppm in natural and waste waters, and up to 50 ppm in soil [5]. The European Union (EU) through the Urban Waste Water Treatment Directive regulated the phosphate level on an annual mean of 1–2 ppm, and the EU Water Framework Directive (WFD) is

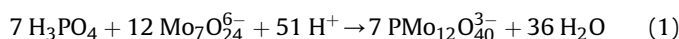
\* Corresponding author.

E-mail address: [fabiana.arduini@uniroma2.it](mailto:fabiana.arduini@uniroma2.it) (F. Arduini).

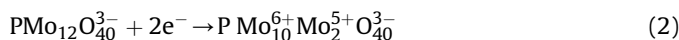
currently being implemented across the EU with the aim of bringing all water bodies up to “good ecological and chemical status” by 2015 with full enforcement of the directive by 2027 [6].

Besides the need to reduce water pollution, sensitive methods for monitoring and evaluation of environmental conditions are required. For this purpose, different analytical methods based on ion chromatography, fluorescence, UV–Vis absorbance, and electrochemistry have been developed [7–11]. Electroanalysis is a solid building block in the analytical field: its strength is certainly attributable to easiness, rapidity, and cost-effectiveness of the measurements. Furthermore, the use of screen-printing technology, combined with portable instrumentation, gives the advantage to decentralize the analysis from “laboratory-dependent” to “laboratory-free”.

Several electroanalytical tools have been reported in literature, exploiting different techniques and electrodes such as amperometric multienzymatic sensors [12], ion selective and membrane enzyme-based electrodes [13], plant tissue electrodes [14], carbon paste electrodes [15], gold rotating disk electrodes [16], cobalt wire electrodes [17], cobalt phthalocyanine-modified screen-printed electrodes [18]. However, the colorimetric method developed by Murphy and Riley [19] remains the most used, and the only one recommended by the Environmental Protection Agency (EPA). This method requires the acidification of the water sample and the addition of a mixture of ammonium molybdate, ascorbic acid, and antimony potassium tartrate to the sample. Phosphate ions, in the presence of molybdate in acidic media, form a P–Mo complex, known as Keggin anion, as reported in Eq. (1):



Subsequently, the addition of ascorbic acid and antimony tartrate reduces the P–Mo complex to a mixed molybdenum oxidation state, as follows (2):



The reduced complex appears blue-colored, and the intensity of the blue color is directly proportional to the amount of phosphate in water. Nevertheless, the effectiveness and sensitivity of this approach suffer from refractive index errors and turbidity interferences [20].

The reduction of the Keggin anion directly at the working electrode without requiring external reducing agents and no interference due to the color of solutions, makes the electroanalytical platform very appropriate to perform the phosphate detection. Our group has recently reported two papers based on screen-printed electrodes (SPEs) modified with carbon black towards water-phosphate detection: the disposable sensor has been effectively utilized in a batch configuration [21], and embedded in a continuous flow system [22]. Simultaneously, Banks' group reported a similar method by using graphite-based SPE to detect phosphate ions in water samples [23]. These methods, despite their great sensitivity and accuracy, require the use of strong acidic media (pH around 1), molybdate ions, and a supporting electrolyte.

Berchmans' and Jonca's research groups reported two alternative methods to detect phosphate without the need of reagent addition. The former has developed a glassy carbon electrode modified with hybrid films based on inorganic molybdate anions trapped in chitosan and ionic liquid for amperometric sensing of phosphate at neutral pH [24]. The latter utilized a multi-compartment electrochemical cell containing a gold working electrode, two molybdenum electrodes to generate molybdate ions, and a proton exchange membrane to provide a high level of  $\text{H}^+$  [25]. Although these methods would represent a simplification in the

operations of the final user, some drawbacks still exist. Solid electrodes need accurate cleaning treatments, the membrane could lack in stability and, mainly, the fabrication technique could be expensive and not really mass producible.

The goal is to develop devices that do not require a skilled operator and do not need expensive and laborious manufacture procedures. Easiness of use, cost-effectiveness, portability and mass-production represent the *leitmotiv* of nascent next-electroanalytical platforms. Paper, thanks to its availability and cost effectiveness, is on top of the list of materials suitable to construct such kind of point-of-need devices [26]. The use of paper is growing step-by-step, finding analytical applications by the production and assembling of optical and electrochemical analytical devices: Whiteside's group [27] and others [28] reported interesting paper-based sensing platforms. Plasma oxidation [29], inkjet-printing [30], and photolithography [31] allow to pattern the paper forming “cellulosic channels” through the establishment of hydrophobic/hydrophilic areas where reagents and analytes can easily diffuse/react/purge before reaching the detector. Solid-ink printing, better known as wax printing, is a helpful and cost-effective alternative in the paper patterning [32], and has been efficiently employed to fabricate microfluidic paper-based analytical devices ( $\mu$ PADs), mainly coupled to a colorimetric detection [33]. However, the use of paper in electroanalytical printed devices is often reported only as an alternative of already existing substrates (polyester), without taking advantage of its fascinating properties. Depending on the grade of paper, its physical characteristics, such as surface area, porosity and thickness, represent a promising tool for fabricating electroanalytical-based assays [34].

In this work we describe, for the first time, an easy and efficient reagent-free paper-based screen-printed electrochemical sensor to detect phosphate ions. Printing electrodes on impregnated paper, containing all reagents necessary for the assay, represent a low-cost and an easy procedure to be carried out by unskilled people. This manufacturing technique has been successfully applied for the determination of phosphate, without the use of additional reagents and by using a very low amount of untreated sample (5  $\mu\text{L}$ ). The proposed configuration has been electrochemically characterized by immobilizing a redox mediator, such as ferricyanide, to evaluate the suitability of the platform. Subsequently, the reagentless paper-based sensor has been analytically characterized, obtaining satisfactory sensor sensitivity, linear range, reproducibility and stability. Furthermore, river water samples were spiked with phosphate and good recoveries have been obtained without any sample treatment and reagent addition. The easy fabrication, as well as the opportunity to realize different configurations, makes this probe useful for different types of electrochemical platforms and different analytes.

## 2. Materials and methods

### 2.1. Reagents and equipments

Potassium ferricyanide, sulfuric acid (95–98%), ammonium heptamolybdate tetrahydrate, potassium chloride, and potassium dihydrogen phosphate were purchased from Sigma–Aldrich (USA). All the solutions were prepared in distilled water. Voltammetric measurements were performed using a portable PalmSens Instrument (PalmSens, Netherlands) in connection with a laptop.

### 2.2. Fabrication of reagentless paper-based electrochemical phosphate sensor

Labor (67  $\text{g}/\text{m}^2$ ) filter paper was purchased from Cordenons (Italy) and used as a substrate for the fabrication of the reagentless

Download English Version:

<https://daneshyari.com/en/article/1162881>

Download Persian Version:

<https://daneshyari.com/article/1162881>

[Daneshyari.com](https://daneshyari.com)