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Original scientific paper

Rapid and sensitive electrochemical determination of phosphate ions using a multi-walled carbon nanotube - carbon paste electrode

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Abstract

Phosphates are widely used in food as texture modifiers, preservatives and flavour enhancers, while excessive intake may negatively affect human health and the environment. Consequently, there is a growing demand for low-cost, portable, and reliable tools for phosphate monitoring in food and water samples. In this work, an electrochemical sensor based on a multi-walled carbon nanotube (MWCNT) modified carbon paste electrode (CPE) was developed for phosphate determination. Phosphate detection was based on the electrochemical reduction of an electroactive phosphomolybdate complex formed in acidic medium (50 mM sulfuric acid). Key analytical parameters, including solution acidity and complexation time, were optimized to enhance sensor performance. Carbon nanotube modification significantly enhanced the electrochemical response. While the bare CPE shows weak, poorly defined redox peaks due to limited electron transfer and low surface area, MWCNT-modified CPE exhibits well-defined peaks with ~6 fold higher current, reflecting improved sensitivity, faster electron transfer, and better peak separation. Using square-wave voltammetry, the sensor exhibited a linear response in the phosphate concentration range of 3.1 to 21.7 mg L^{-1}, with a detection limit of 0.03 mg L^{-1} and a response time of approximately 10 s. The sensor was successfully applied to real sausage samples, yielding recoveries of 94.6 to 97.2 % with relative standard deviation values below 5 %. The presented MWCNT-CPE sensor provides a cost-effective, portable and simple device for fast and reliable in situ detection of phosphate in food and water samples.

Keywords

Phosphate anion sensing; nanomaterial-modified electrode; phosphomolybdate complex; voltammetric methods; real food samples

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Introduction

Inorganic phosphate is a salt of phosphoric acid found as the negatively charged mineral ion, or organophosphate, in many living systems [1]. Phosphate, being the primary inorganic form of phosphorus, serves as an important structural and functional component to all aquatic organisms. However, when abundant, it is an important cause of eutrophication, inducing algal blooms and deteriorating water quality [2-4]. Its dual role is also highlighted in food and the agricultural system, where phosphate is important for both DNA and ATP synthesis and plant nutrition, but high levels are toxic to plants [5-8].

Apart from environmental issues, phosphorus consumption has evolved as an increasing public health concern. The amounts of phosphate in the diet and serum are important health issues, not only for CKD (chronic kidney disease) patients, a high-risk group for dysregulated phosphate, but also healthy individuals, as accumulating evidence suggests excessive phosphorus intake can disturb metabolism, cardiovascular health and bone strength. Recent studies indicate that in healthy individuals with normal renal function, dietary phosphate is a modifiable source of health risk [9,10].

Overuse of organic phosphates in food, particularly in ultra-processed foods (UPFs), has been linked to pathways that raise risk for the progression and mortality from renal and cardiovascular diseases. More and more such discoveries cast doubt on the safety and, indeed, the current regulatory status of phosphate additives, although it may be difficult to conclusively demonstrate causality under contemporary consumption patterns [11,12].

Given the environmental and health issues related to such substances, accurate determination of phosphate in several sample matrices remains essential. A variety of methods have been developed for determining total phosphorus, including high-performance liquid chromatography (HPLC) and ion chromatography, owing to their excellent selectivity and accurate quantification [13]. Fluorescence-based techniques present excellent sensitivity and selectivity and are suitable for trace analysis [14]. Moreover, spectrophotometric procedures are widely used because they effectively measure phosphorus content in various sample matrices [15-17]. Among the spectrophotometric methods, the phosphomolybdenum blue (PMB) method is widely used for the determination of dissolved phosphate. The procedure is based upon the formation of the Keggin anion of PMB by reaction between ammonium molybdate, ascorbic acid and antimony potassium tartrate under acidic conditions. Nevertheless, spectrophotometric techniques suffer from interferences, instability of reagents and sample preparation is time-consuming, especially in complex food matrices. Electrochemical methods present a compelling alternative, as they are less sensitive to matrix interference and more selective, in comparison with other techniques for gathering data on phosphomolybdate ions-based assays [2,18], because of the electrode-surface reaction.

Talbi *et al*. [19] reported that several electrochemical approaches have been developed for phosphate detection. These methods have ranged from the indirect detection of phosphates through metal-phosphate complexes, such as with Ag, Co and Mo [20-22] to sensors heavily involving an array of nanomaterials like metals [23], metal oxides [24], nanoparticles [25], nanorods, nanowires [26] and carbon nano-materials [27,28]. The carbon nanomaterial-based electrochemical sensors have demonstrated significant enhancement in electrocatalytic performance, leading to higher selectivity, sensitivity and lower detection limits by means of a good surface area-to-volume ratio and electrochemical property. Among these materials, carbon nanotubes (CNT), especially multiwalled structure (MWCNT) have been focused on because of their excellent conductivity, great specific area, chemical stability and good electrocatalytic activity. The properties of these materials have therefore made them promising candidates for nano-materials to improve the performance of electrochemical sensors [29]. For instance, sensors incorporating MWCNT-reinforced CdS/g-C_3N_4 nanocomposites have demonstrated remarkable recovery percentages for the detection of paraquat in real water samples [30,31].

The objective of this research is to develop and apply an inexpensive, small-sized and sensitive electrochemical sensor based on MWCNT-CPE for the possible analysis of phosphate in food samples and natural water samples. The analytical conditions, such as complexation time and supporting electrolyte, are optimized to achieve better sensitivity, stability and reproducibility. This study aims to construct a fast, field-deployable device that provides real-time quantification of phosphate for on-site applications in food and environmental monitoring.

Experimental

Reagent and chemicals

Analytical-grade reagents and materials for all experiments were from Sigma-Aldrich (St. Louis, MO, USA) and Merck (Merck KGaA, Darmstadt, Germany). A high-purity phosphate standard (PO_4^{3-}) KH_2PO_4, was supplied by Carlo-Erba (Milan, Italy) and stored at 4 °C to maintain stability. Furthermore, a recently prepared stock solution of ammonium molybdate (0.1 mmol L^{-1}) was prepared from high-purity reagents and stored at 4 °C to avoid decomposition. All solutions were prepared in double-distilled water to obtain the highest purity and reproducibility. The supporting electrolyte solutions were prepared with H_2SO_4 and HNO_3 (99 % *p.a.* Merck KGaA, Darmstadt, Germany). Potassium chloride (KCl) for electrolytes was obtained from Sigma-Aldrich (St. Louis, MO, USA). Synthetic graphite powder (71 to 90 µm) was obtained from Alfa Aesar (99.9 % purity, Haverhill, MA, USA), and paraffin oil (Olio di Vaselina) was purchased from Zeta Farmaceutici (Sandrigo, Italy) for electrode modification. To improve electrochemical performance, MWCNTs with outer diameters of 10 to 20 nm and lengths of 0.5 to 2 µm were used as nanomodifiers for the electrode material. All the reagents were kept and manipulated under standard laboratory conditions to avoid errors and maintain reproducibility of experimental results.

Apparatus

All electrochemical measurements were performed with a PalmSens4 potentiostat-galvanostat (PalmSens BV, Houten, The Netherlands), wirelessly connected to a personal computer using Bluetooth and controlled *via* software dedicated to the three-electrode system. The fabricated modified MWCNT-CPE sensor was employed as the working electrode, a platinum wire (Sigma-Aldrich, St. Louis, MO, USA) as the counter electrode, and a silver/silver chloride in KCl (3 M) (Metrohm AG, Herisau, Switzerland) as the reference electrode. The detection of the phosphate ions (PO_4^{3-}) was based on an electrochemical method by employing different electrochemical techniques such as cyclic voltammetry (CV), square wave voltammetry (SWV), differential pulse voltammetry (DPV) and chrono-amperometry (CA). These electrochemical techniques were used to study the electrochemical behaviour of phosphate species and to evaluate the analytical performance of the sensor.

Electrode preparation

Preparation of bare carbon paste electrode

The carbon paste electrode (CPE) was fabricated by combining 1.00 g of graphite powder (particle size 72 to 90 µm) with 300 µL of paraffin oil. The mixture was kneaded thoroughly to form a consistent, pliable paste. This paste was then filled into a 2 mL insulin syringe, which served as the electrode housing, and a copper wire was inserted to establish an electrical connection. Before use, the top paste layer of the electrode was levelled and polished on a clean glass plate to ensure smoothness and reproducibility.

Preparation of multi-walled carbon nanotube-modified carbon paste electrode

To fabricate the MWCNT-CPE nanocomposite, 0.100 g of MWCNTs was combined with 1.00 g of graphite powder (particle size 70 to 90 µm), as optimized in previous work [32,33]. Then, 300 µL of paraffin oil was added, and the mixture was kneaded for 30 minutes to produce a uniform, cohesive paste. To ensure proper immobilization of the MWCNTs within the carbon matrix, the composite paste was stored at 4 °C for 24 hours prior to use. The stabilized paste was then packed into a plastic syringe (internal diameter 8 mm, outer diameter 9.5 mm) to serve as the electrode body. Before electrochemical measurements, the electrode surface was polished on a glass plate to obtain a smooth, uniform surface.

Sample preparation

Different processed meat products were randomly purchased from local markets in Tirana. Samples were crushed and homogenized, and the mixture obtained was divided into several aliquots and kept frozen until the day of treatment. 1 g aliquot of the homogenized sample was weighed into pre-cleaned Teflon pans. Finally, 5 ml of nitric acid (HNO_3, 67 to 69 %, ultrapure, Carlo Erba) and 1 ml of hydrogen peroxide (H_2O_2, 35 %) were added. Then, the Teflon containers were left uncovered for 1 to 2 h to complete the reaction and allow the evolved vapours to evaporate. The sealed containers were then digested in a microwave system (Berghof, Speed Wave MWS-3+) at 190 °C and 30 bar for 10 min. After digestion, the samples were cooled to room temperature before further analysis. Samples were cooled down at room temperature after digestion. Finally, samples were transferred quantitatively into 50 mL calibrated flasks and made up to volume with bidistilled water. The standard solution 150 ppm PO_4^{-3} was prepared by accurately weighing a known amount of KH_2PO_4 and dissolving it in a specified volume of distilled water. The solution was poured into a volumetric flask, then diluted to volume with bidistilled water and mixed to equilibrate the final concentration.

Electrochemical analysis

Electrochemical techniques offer a simple and easily miniaturized alternative for phosphate determination, making them suitable for field and remote sensing applications. In this study, differential pulse voltammetry (DPV), cyclic voltammetry (CV), square-wave voltammetry (SWV), and chronoamperometry (CA) were employed to investigate the electrochemical behaviour of phosphate species and their interactions with modified carbon paste electrodes.

Electrochemical phosphate detection was performed by forming an electroactive phosphor-molybdate complex, in which molybdate ions act as a selective complexing agent. The resulting complex generates a distinct electrochemical signal directly proportional to the phosphate concentration. Measurements were conducted in 50 mM H_2SO_4 using CV, DPV, SWV and CA. CV and DPV were recorded at a scan rate of 100 mV s^{-1}, SWV employed a pulse amplitude of 0.05 V and a frequency of 30 Hz, and CA responses were measured at a fixed potential of -0.3 V. Prior to phosphate addition, a stoichiometric amount of 0.1 mM molybdate solution was introduced to ensure controlled complex formation, and the analytical signal was defined as the current change resulting from the phosphomolybdate formation.

Results and discussion

Phosphomolybdate complex behaviour at bare carbon paste electrode and multi-walled carbon nanotube- carbon paste electrode

The electrochemical behaviour of phosphate ions at the electrode surface was investigated by studying the response of both unmodified CPE and MWCNT-CPE in an acidic medium (50 mM H_2SO_4) containing 1 mL of 0.1 mM molybdate at a phosphate ion concentration of 3.1 mg L^{-1} using cyclic voltammetry. A potential sweep was initiated in the positive direction (+0.8 to -0.2 V), followed by a reverse scan to promote the reduction of the phosphomolybdate complex and generate a measurable electrochemical signal. Cyclic voltammograms obtained under these conditions are presented in Figure 1.

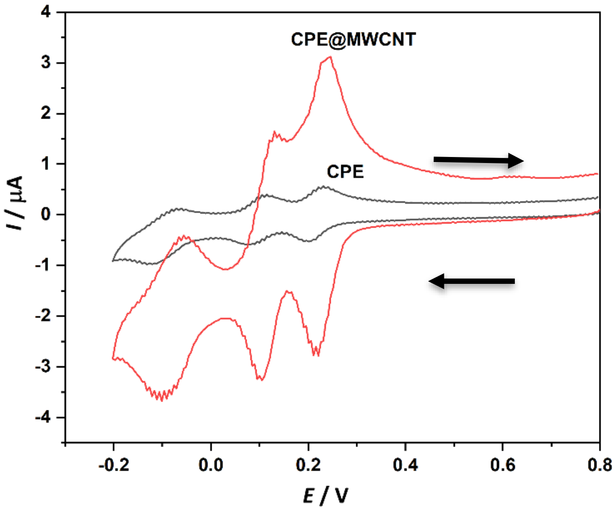

Figure 1. *Cyclic voltammograms recorded using bare CPE and MWCNT-CPE in 50 mM H_2SO_4 (pH 1.3), containing 0.1 mM molybdate in the presence of 3.1 mg L^{-1} phosphate ions at a scan rate of 100 mV s^{-1}*

As illustrated in Figure 1, the bare CPE exhibits weak and poorly defined redox peaks, reflecting limited electron transfer and low effective surface area for the formation of the electroactive phosphomolybdate complex. In contrast, the MWCNT-modified electrode exhibits significantly higher peak currents and improved peak separation, indicating enhanced electron-transfer kinetics and greater reversibility. Two well-defined redox couples appear around 0.1 and 0.3 V, corresponding to the surface-confined redox processes of the phosphomolybdate complex, consistent with previous studies reporting the catalytic effect of carbon nanotubes in phosphate detection [2,18].

Electrochemically, the improvement can be attributed to the high conductivity and large surface area of MWCNTs, which facilitate rapid electron transfer between the phosphomolybdate species and the electrode surface and provide additional active sites for adsorption. This results in a higher faradaic current and more distinct redox peaks, demonstrating the electrocatalytic role of MWCNTs in enhancing sensitivity. Similar enhancements have been reported in other nanocarbon-based sensors, where modification with CNTs or graphene significantly improved the detection of phosphate and other anions via surface-confined redox reactions [27,28]. Overall, these results indicate that MWCNT modification substantially improves the electrochemical performance of CPE, making it a more sensitive and reliable platform for phosphate quantification at relevant concentrations in aqueous and food matrices.

Based on the enhanced redox activity and improved reversibility observed at the MWCNT-CPE surface, further studies focused on optimizing the experimental parameters that affect the electrochemical response of phosphate.

Optimization of the experimental conditions for phosphate detection

Effect of complexation time

Since the electrochemical response of phosphate relies on the formation of an electroactive phosphomolybdate complex, the effect of complexation time was first investigated. The influence of complexation time on the electrochemical response of phosphate was evaluated by monitoring the peak current of the phosphomolybdate complex at interaction times from 60 to 420 s, with a constant phosphate concentration (5.9 mg L^{-1}).

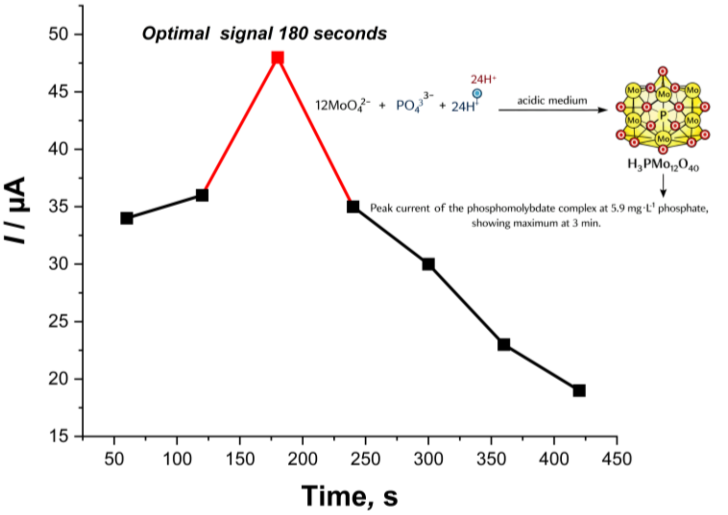

Figure 2. *Effect of complexation time on the SWV peak current of the phosphomolybdate complex at a phosphate concentration of 5.9 mg L^{-1}, in 15 mL of 50 mM H_2SO_4, with 1 mL of 0.1 mM ammonium molybdate. SWV measurements were performed with an amplitude of 50 mV and a frequency of 30 Hz*

As shown in Figure 2, the peak current of the phosphomolybdate complex increased during the initial stages of complexation, reaching a maximum at 180 s. Beyond this time, the peak current decreased, suggesting that prolonged complexation does not enhance the signal. This decrease may be due to partial hydrolysis, structural rearrangement, or surface saturation of the complex, which limits electron transfer efficiency. Therefore, 180 s was selected as the optimal complexation time.

The observed time-dependent behaviour is consistent with previous studies on electrochemical phosphate sensing, where surface effects and complex stability were critical [2]. Mechanistically, the electroactive phosphomolybdate complex forms through coordination of phosphate anions to molybdenum centres under acidic conditions, facilitating electron transfer and generating the measurable voltammetric signal. Moreover, molybdenum-based sensors have shown that strong coordination between phosphate anions and molybdenum centres produces well-defined redox signals, highlighting the importance of optimizing interaction time for robust electrochemical responses [34].

Effect of supporting electrolyte

Following the optimization of the complexation time, the influence of the supporting electrolyte composition and acidity on the electrochemical response was systematically evaluated.

The influence of the supporting electrolyte on the electrochemical response of the phosphomolybdate complex was investigated using various acidic media, including H_2SO_4 at 50, 100, and 500 mM, HCl 100 mM, and a mixture of H_2SO_4 100 mM with KCl 10 mM, with a constant phosphate concentration of 11.6 mg L^{-1}. The estimated pH values of the supporting electrolytes were approximately 1 for HCl and 1.22, 0.95 and 0.29 for 50, 100 and 500 mM H_2SO_4. Adding KCl does not affect the pH; it only affects ionic forces. As shown in the SWV measurements (Figure 3), the peak current was highly dependent on both the electrolyte type and concentration. Among the tested conditions, 50 M H_2SO_4 yielded the most intense and well-defined reduction peak, reflecting optimal proton availability and a moderate ionic strength that promotes efficient complex formation and electron transfer. Higher acid concentrations, the addition of salts, or the use of alternative acids resulted in lower or broader peaks, likely due to partial perturbation of the complex, altered electron-transfer kinetics, or changes in solution conductivity.

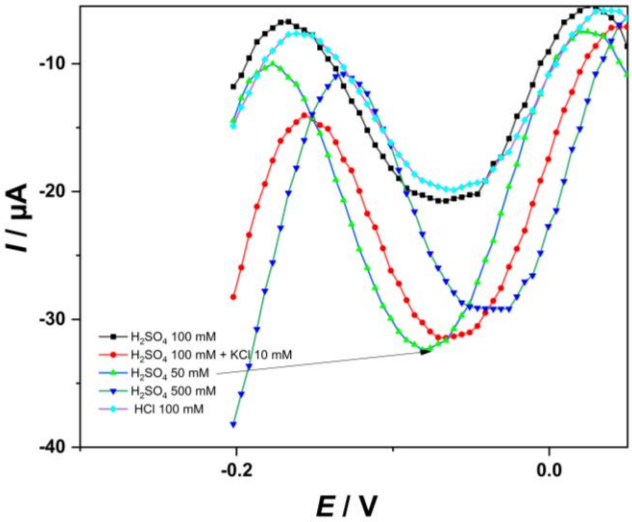

Figure 3. *Effect of the supporting electrolyte on the reduction current of 11.6 mg L⁻¹ phosphate using MWCNT-CPE sensor in different electrolytes containing 0.1 mM ammonium molybdate. pH values were approximately 1 for HCl and 1.22, 0.95 and 0.29 for 50, 100, and 500 mM H_2SO_4, respectively, while addition of KCl did not affect pH but only ionic strength. SWV measurements were performed with an amplitude of 50 mV and a frequency of 30 Hz*

These observations are consistent with previous studies indicating that optimal supporting electrolyte conditions enhance electron transfer and reduce background current, whereas excessive ionic strength or highly acidic conditions can hinder the electrochemical response [2,34,35]. Therefore, 50 mM H_2SO_4 was selected as the supporting electrolyte for all subsequent measurements, ensuring sensitive and reproducible phosphate detection.

Analytical performance of the multi-walled carbon nanotube- carbon paste electrode sensor for phosphate detection

Voltammetric and amperometric detection of phosphate at multi-walled carbon nanotube- carbon paste electrode

The electrochemical detection of phosphate at the MWCNT-CPE sensor is based on the formation of a molybdate-phosphate complex under acidic conditions (50 mmol L^{-1} H_2SO_4, 0.1 mmol L^{-1} molybdate). In an acidic medium, phosphate reacts with molybdate ions to form a heteropoly complex known as phosphomolybdic acid with a Keggin structure. The resulting redox-active phosphomolybdate complex can be electrochemically reduced at the electrode surface, generating the voltammetric or amperometric signal used for phosphate determination. The formation of the phosphomolybdate complex can be described by Reaction (1) [2,18,36]:

$$PO_4^{3-} + 12MoO_4^{2-} + 24H^+ \rightarrow H_3PMo_{12}O_{40} + 12H_2O \quad (1)$$

The analytical performance of the MWCNT-CPE sensor was systematically investigated using SWV, DPV, and amperometry. The combination of these complementary electroanalytical techniques provides a robust evaluation framework, enabling validation of the sensor response and analytical parameters across different electrochemical operating conditions.

Figure 4 presents the electrochemical responses of the sensor toward increasing phosphate concentrations under identical acidic conditions. SWV responses (3.1 to 19.6 mg L^{-1}, Figure 4A), DPV responses (3.1 to 10.4 mg L^{-1}, Figure 4B), and amperometric responses at a fixed potential of -300 mV (3.1 to 15.6 mg L^{-1}, Figure 4C) demonstrate that all three techniques provide linear responses, although with distinct current profiles and linear ranges. The measured currents are expressed in μA and correspond to background-corrected signals.

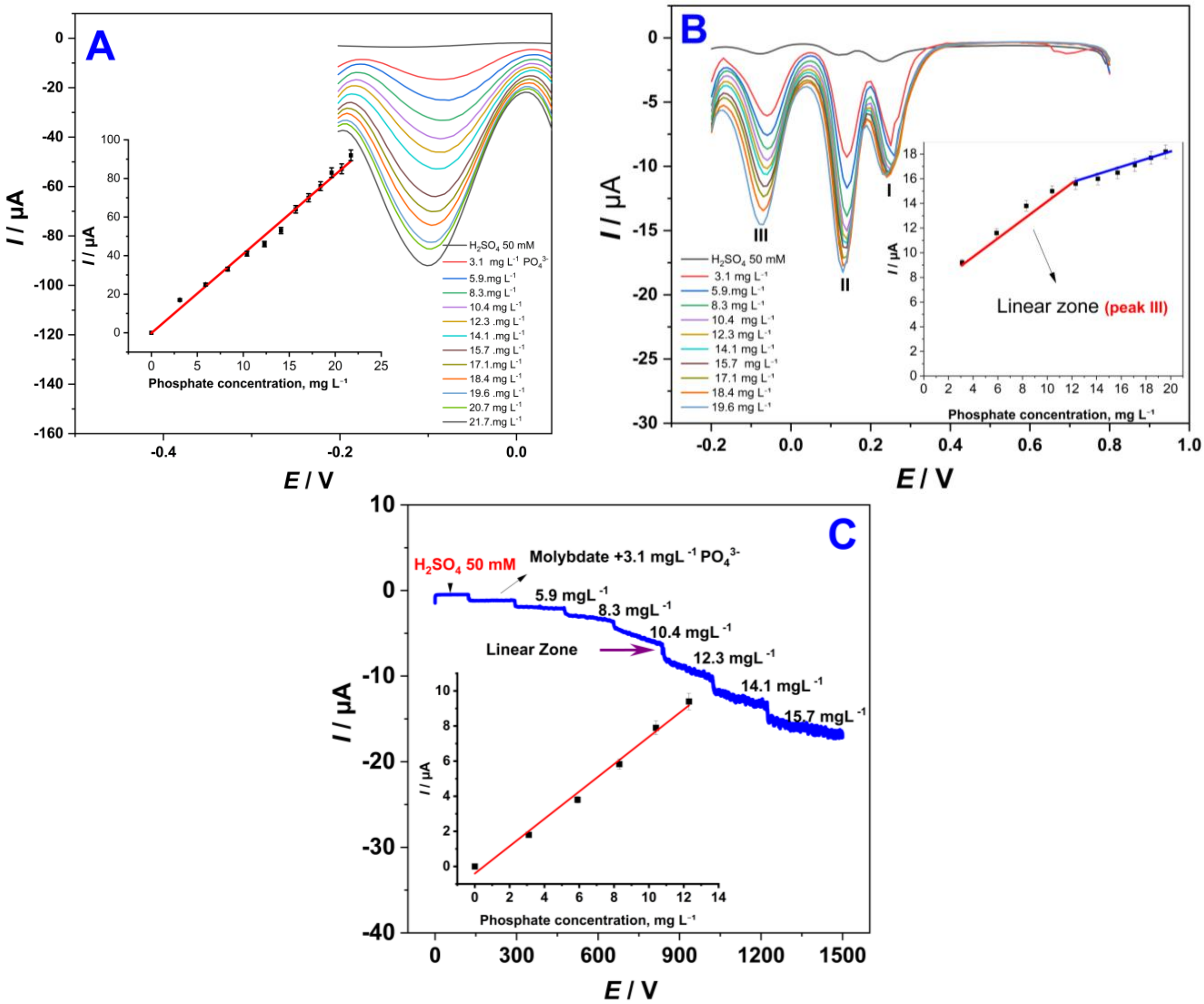

Figure 4. *Electrochemical responses of the MWCNT-CPE sensor for phosphate detection recorded under identical acidic conditions (50 mmol L^{-1} H_2SO_4, 0.1 mmol L^{-1} molybdate): A) SWV responses for increasing PO_4^{3-} concentrations (3.1 to 21.7 mg L^{-1}), B) DPV responses under PO_4^{3-} concentrations (3.1 to 19.6 mg L^{-1}) and C) amperometric response at 300 mV for PO_4^{3-} concentrations ranging from 3.1 to 15.6 mg L^{-1}. Insets in all panels show the corresponding calibration curves (*n*=3) in the linear concentration range*

Insets in each panel show the corresponding calibration curves for peak current, μA *vs.* phosphate concentration, mg L^{-1}. The calibration curves for SWV, DPV, and amperometry were constructed using 6 to 7 standard phosphate concentrations within the reported ranges. Error bars represent the standard deviation of replicate measurements (n = 3).

The voltammetric and amperometric responses presented in Figure 4 demonstrate that phosphate detection at the MWCNT-CPE electrode is strongly influenced by the selected electrochemical technique. While SWV, DPV, and amperometry all produce linear responses toward phosphate concentration, their current profiles, peak definition, and working ranges differ significantly. The analytical parameters derived from the calibration curves further highlight the distinct characteristics of each electrochemical technique (Table 1).

Table 1. *Analytical comparison of electrochemical techniques for phosphate detection using the MWCNT-CPE sensor*

Technique	Linear range, mg L^{-1}	Calibration equation	Sensitivity, µA (mg L^{-1})$^{-1}$	R^2	LOD, mg L^{-1}	RSD*, %
SWV	3.1 to 21.7	$I = 4.1085C - 0.181$	4.1085	0.9917	0.030	1.65
DPV	3.1 to 10.4	$I = 0.8102C + 6.7895$	0.8102	0.9929	0.022	1.88
Amperometry	3.1 to 10.4	$I = 0.7673C + 0.3526$	0.7673	0.9906	0.083	4.1

*RSD values were obtained from five successive measurements (*n*=5) at 5.9 mg L^{-1} phosphate.

From the data summarized in Table 1, SWV exhibits the widest linear range (3.1 to 21.7 mg L^{-1}) and the highest sensitivity (4.1085 µA (mg L^{-1})$^{-1}$), indicating efficient electron transfer at the MWCNT-CPE interface and enhanced faradaic current generation. The well-defined SWV peaks and broad working range make this technique particularly suitable for quantitative analysis of phosphate in real samples. DPV, while showing lower sensitivity (0.8102 µA (mg L^{-1})$^{-1}$) and a narrower linear range (3.1 to 10.4 mg L^{-1}), maintains excellent linearity (R^2 = 0.9929) and provides sharp, well-resolved peaks.

Amperometric detection also demonstrates good linearity (3.1 to 10.4 mg L^{-1}, R^2 = 0.9906), although with slightly lower sensitivity (0.7673 µA (mg L^{-1})$^{-1}$). This technique offers rapid and stable current responses suitable for real-time monitoring, although it is less sensitive for trace-level quantification. The high linear correlation coefficients indicate a good linear relationship between current response and phosphate concentration within the studied ranges.

The limits of detection (LOD) were calculated using the expression LOD = 3σ/S, where σ represents the standard deviation of the blank signal (*n* = 3) and S is the slope of the calibration curve. For SWV, the calculated LOD was 0.03 mg L^{-1}. The repeatability of the proposed sensor was evaluated by performing five successive measurements (*n*=5) of a phosphate solution at 5.9 mg L^{-1} under identical experimental conditions. The obtained relative standard deviation (RSD) was 1.65 % for SWV, indicating good intra-day repeatability of the electrochemical response. DPV and amperometric measurements also exhibited satisfactory analytical performance, with LOD values of 0.022 and 0.083 mg L^{-1} and repeatability, as measured by RSD, of 1.88 and 4.1 %, respectively. These results demonstrate the good reproducibility of the sensor response across different electrochemical techniques, with all measurements performed using the same modified electrode under identical experimental conditions.

Overall, the combined evaluation of linear range, sensitivity, LOD, and repeatability indicates that SWV is the most suitable technique for phosphate quantification in real samples. Its superior sensitivity, broader linear range, and well-defined peaks make it the preferred method for practical applications, while DPV and amperometry serve as complementary techniques demonstrating the versatility of the MWCNT-CPE sensor.

Comparison of analytical performance of different electrochemical sensors for phosphate determination

In Table 2, the analytical performance achieved in this work compares favourably with previously reported phosphomolybdate-based electrochemical sensors. Although some literature methods report lower detection limits, they often rely on complex electrode architectures or costly fabrication procedures. In contrast, the MWCNT-CPE sensor developed in this study combines a low micromolar detection limit with a wide linear range, simple electrode preparation, and cost-effective materials, making it particularly attractive for routine phosphate analysis in aqueous samples.

Table 2. *Comparison of analytical performance of different electrochemical sensors for phosphate determination*

Sensor type	Detection technique	LOD, mg L^{-1}	Linear range, mg L^{-1}	Ref.
Boron-doped diamond (BDD) electrode	SWV	0.004	0.02 to 3	[35]
Carbon screen-printed electrode (CSPE) modified with CuPc/MWCNT	SWV	0.109	0.95 to 9.5	[19]
Flexible electrode with electrodeposited MoOx film	SWV	0.76	0.95 to 94.97	[34]
All-solid-state Cu electrode (ISE)	Potentiometry	0.095	0.95 to 9497	[37]
Glassy carbon electrode modified with PPy/CNR/MoO_2	DPV	0.0142	0.28 to 101.1	[38]
Glassy carbon electrode modified with ferrioxalate complex	CV	0.042	0 to 0.071	[39]
Copper electrode modified with Co-Ni alloy layer	Potentiometry	0.095	0.095 to 9497	[40]
Nickel electrode modified with nickel oxide (NiO) layer	Amperometry	9.5×10^{-6}	9.5×10^{-6} to 0.0095	[24]
MWCNT-CPE	SWV	0.78	3.1 to 21.7	This work

The use of a carbon paste electrode modified with MWCNTs further enhances the practicality of the sensor by enabling easy surface renewal and reproducible fabrication, key advantages over conventional solid electrodes.

Reproducibility and stability of the multi-walled carbon nanotube- carbon paste electrode

The reproducibility of the MWCNT-CPE sensor was assessed by performing SWV measurements in 11.6 mg L^{-1} phosphate solutions using three independently prepared electrodes. The relative standard deviation (RSD) of the reduction peak current was 4.0 %, indicating excellent consistency across different electrodes and minimal variation in the electrochemical response.

The long-term stability of the MWCNT-CPE sensor was evaluated by monitoring the anodic peak current at 3.1 mg L^{-1} phosphate under intermittent measurement conditions. The modified electrodes were stored at 4 °C in a refrigerator when not in use, and their long-term stability was evaluated over 36 days. The recorded current responses ranged from 22.6 to 26.0 µA, with an average value of 24.2 µA. The relative standard deviation (RSD) was calculated to be 5.3 %, indicating acceptable signal reproducibility over prolonged storage [41,42]. Notably, the sensor retained approximately 97.5% of its initial current response after 36 days, demonstrating good temporal stability of the electrochemical platform.

Application of the multi-walled carbon nanotube- carbon paste electrode sensor to real sausage samples

The applicability of the proposed MWCNT-CPE sensor was evaluated using three randomly selected sausage samples purchased from local markets. For each sample, 50 µL of homogenized sausage extract was added to a measurement cell containing 15 mL of 50 mM H_2SO_4 and 1 mL of 0.1 mM ammonium molybdate solution. Phosphate quantification in the samples was performed using the standard addition method to account for potential matrix effects. In this approach, known amounts of phosphate were added directly to the sample aliquots (spiked samples), and the resulting SWV responses were recorded. This method ensures accurate determination of phosphate concentrations in complex food matrices such as processed meat products.

Phosphate concentrations in the sausage samples were determined from standard addition plots, with recovery values ranging from 94.6 to 107 % (Table 3). The slightly lower recovery observed for Sausage 3 at the lower spike level (94.6 %) likely reflects minor matrix effects. At higher phosphate concentrations, recoveries stabilized between 96 and 107 %, demonstrating the good accuracy and reliability of the MWCNT-CPE sensor in these complex food matrices.

Table 3. *Phosphate recovery of the MWCNT-CPE electrode in real sausage samples using SWV*

Sample	Amount, mg L^{-1}		Recovery, %	RSD, % (n = 3)
	Added	Found		
Sausage 1	9.3	9.99	107	2.3
	14.5	14.0	96	3.9
Sausage 2	9.3	8.8	95	2.5
	14.5	14.1	97	2.8
Sausage 3	9.3	8.8	94.6	5.1
	14.5	14.1	97.2	4.9

Figure 5 shows representative SWV voltammograms of a sausage sample, measured before and after successive spiking with phosphate standard solutions.

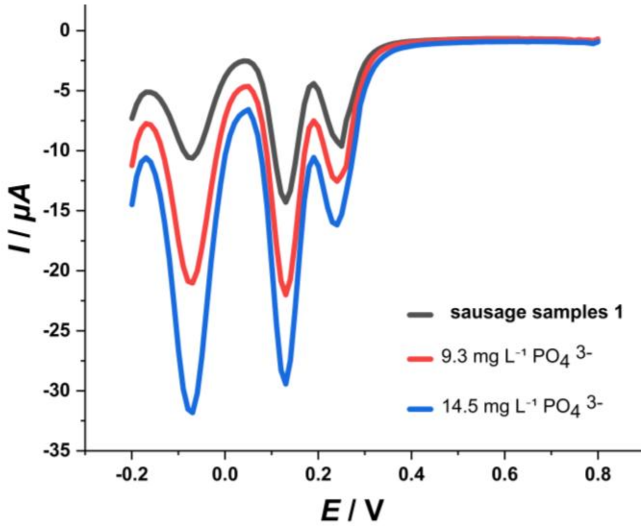

Figure 5. *Square wave voltammograms recorded for a sausage sample before and after successive phosphate additions at 9.3 and 14.5 mg* L^{-1}

The peak current increased progressively with each addition, while the peak potential remained stable. The well-defined reduction peak confirms that the phosphate signal is electrochemically distinguishable and reliably preserved in the complex matrix of the sausage samples.

The satisfactory recovery values obtained for all tested sausage samples confirm that the MWCNT-CPE sensor can accurately quantify phosphate in real food samples. The standard addition method effectively compensates for potential matrix effects, while the high selectivity of the phosphomolybdate system ensures reliable signal generation even in the presence of potential interfering components such as proteins, lipids, and other additives commonly found in processed meat products. Unlike individual interference tests with single ions, the standard addition approach evaluates the sensor performance directly within the real sample matrix, providing a more realistic assessment of analytical selectivity under practical conditions. The obtained recoveries (94.6-107%) indicate that these matrix components do not significantly affect the electrochemical response of the phosphomolybdate system. Compared to conventional spectrophotometric or chromatographic methods, this approach offers significant advantages, including minimal sample preparation, rapid analysis, and low operational cost, highlighting the potential of the MWCNT-CPE sensor for routine monitoring of added phosphates in processed meats.

Conclusions

The MWCNT-CPE sensor developed in this work provides a sensitive, reproducible, and rapid platform for phosphate detection. Optimization of acidity and complexation time ensured formation of a stable phosphomolybdate complex, while carbon nanotube modification enhanced electron transfer and active surface area. Square-wave voltammetry offered the highest sensitivity and widest linear range (3.1 to 21.7 mg L^{-1}) with a low detection limit of 0.03 mg L^{-1}. Successful application to real sausage samples, with recoveries of 94.6 to 97.2 % and RSD <5 %, confirms its reliability in complex food matrices. Combining low cost, simple preparation, portability, and fast response, this sensor represents a practical and versatile tool for on-site phosphate monitoring, with potential for extension to other analytes and environmental samples.

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