

Phosphate Detection in Water: a Potential Amperometric Approach

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The reduction of phosphate on a diamond electrode has been demonstrated opening the way to a possible direct amperometric phosphate detection. Preliminary results show a linear response in the ppm range. Applications are foreseen in the environmental control.

Excess phosphorus causes eutrophication (excess of nutrient promoting a proliferation of plants, (especially algae) in ecosystems. Consequently, the monitoring of phosphate in waste, drinking and natural water is of major importance. There is a strong interest in a method alternative to the standard molybdate colorimetric method, which is not well suited to continuous monitoring under field conditions. Various potentiometric ion-selective electrodes, amperometric and potentiometric enzyme-electrodes have been studied but so far without achieving results suitable for application under real conditions^[1].

Synthetic thin film boron doped diamond (BDD) electrodes are known to have a large over-potential for water oxidation or reduction^[2]. Species that cannot be efficiently oxidized or reduced on conventional electrodes, due to the predominant oxidation or reduction of water, are susceptible to undergo an electrochemical reaction on boron-doped diamond. Furthermore BDD has a very low and stable voltammetric background current and high stability under strongly oxidizing conditions. These properties have already been exploited for the detection of various organic or inorganic analytes^[3].

The objective of this work was therefore to evaluate the possibility to take advantage of the specific BDD characteristics to measure phosphorous by direct amperometric detection.

Preliminary characterization of orthophosphate electro-chemical properties was done by cyclic voltammetry. Tests were done in deaerated phosphate solutions at pH 7 on a rotating diamond disk electrode with a platinum counter electrode and an Ag/AgCl/KCl 3 M reference electrode.

Figure 1 shows the current measured during the forward scan at several high phosphate concentrations. The reduction wave induced by orthophosphate addition is clearly visible, starting at ca. -1.2 V. The assumed reaction on the BDD electrode is the reduction of P(IV) to P(III). Figure 1 indicates that the diffusion limited current is however not reached before the onset of water reduction as shown by the baseline curve at 0 ppm phosphorous.

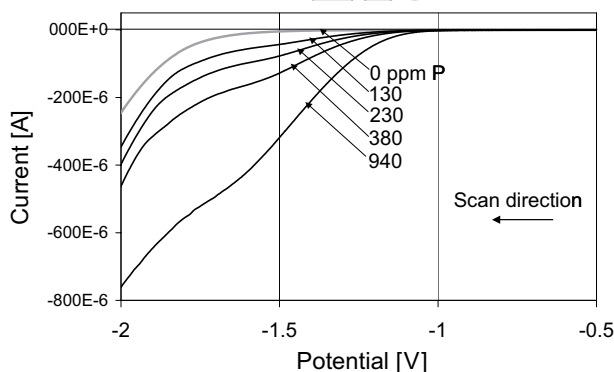


Figure 1: Reduction of phosphate: voltammetry in pH 7 deaerated 50 mM KCl solution, 1000 rpm rotating BDD electrode, scan rate 100 mV/s; P added as $\text{Na}_2\text{HPO}_4 + \text{KH}_2\text{PO}_4$.

Figure 2 shows that the reduction current, measured at a potential of -1.5 V, is well correlated to the phosphate concentration in a range from 5 to 1000 ppm. The estimated detection limit of 2 ppm is still high due to the relatively important residual current at -1.5 V, partly resulting from residual dissolved oxygen reduction and partly from the on-set of water reduction.

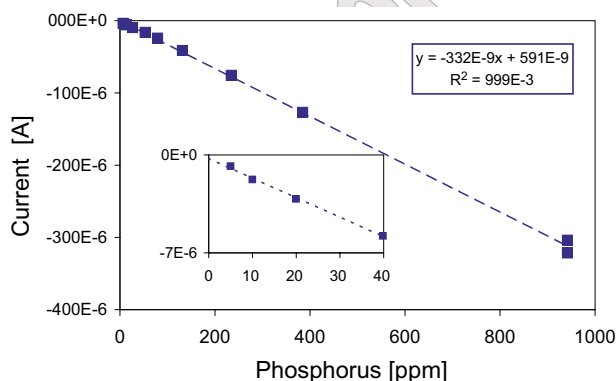


Figure 2: Phosphorous reduction current at -1.5V vs. concentration.

In conclusion, direct phosphate reduction on BDD electrode has been demonstrated, opening the possibility for the development of an amperometric sensor. The presently achieved detection limit restricts its application to monitoring wastewater containing higher levels of phosphorous. A major improvement of the detection limit will be needed for surface water analysis. Further work should also address the issue of measurements in real water samples including potential interferences.

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