

Electrochemical Phosphate Sensor (OTT ID 1513)

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Increased levels of phosphates can lead to:

- Eutrophication (excessive plant growth such as algal blooms)
- At first plant growth may be stimulated, but over time excessive plant growth can choke the water way, and lead to death of the plants
- Low oxygen in waterways can occur and death of aquatic organisms
- Some algal blooms are toxic to humans

Sources of increased phosphates in the environment include:

- Fertilizers and farm water run-off (and manufacturing of fertilizers)
- Sewage
- Pulp and paper industry
- Detergents
- Vegetable and fruit processing





- The EPA notes that "Monitoring phosphorus is challenging because it involves measuring very low concentrations down to 0.01 milligram per liter (mg/L) or even lower...."
- Even such very low concentrations of phosphorus can have a dramatic impact on streams. Less sensitive methods should be used only to identify serious problem areas.
- The EPA approved method for measuring phosphates involves the use of chemical reagents
- In some cases samples must be brought back to the lab for analysis



Our inventors developed a disposable low-cost SPE phosphate sensor using Graphene Oxide, Pyrrole, Ammonium molybdate and Cobalt Oxide

- Sensitive Detects as low as 10⁻¹⁰ M (mol/L), several orders of magnitude lower than other devices
- **Inexpensive** Only a <u>voltmeter</u> is needed for detection and the materials used are readily available
- Disposable Sensors can be fabricated for one time use for quick and easy set-up
- Pre-Calibrated Sensors can be supplied pre-calibrated and are easy to use
- **Multiple Applications** Residential, industrial, environmental, governmental and research use

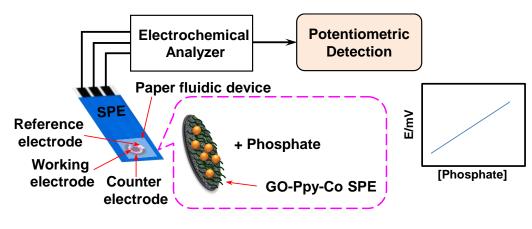


- U.S. Provisional Patent Application filed August 2017
- Looking for a development partner to:
 - Aid in development of the final end user prototype
 - Determine the proper manufacturing pathway
 - Aid in funding further evaluation of the sensors for long term use versus disposable
 - Bring the products to market
- Market
 - The global market for water analysis instrumentation is projected to reach \$3.6 billion by 2020
 - Water analysis is critical in residential, commercial, and industrial sectors



Novel Disposable Phosphate Sensor

Schematic diagram of the setup



Chemical reaction using Cobalt (example)

 $3CoO + 2H_2PO_4^- + 2H^+ \rightleftharpoons Co_3(PO_4)_2 + 3H_2O \text{ at pH 4.0}$ $3CoO + 2HPO_4^{2-} + H_2O \rightleftharpoons Co_3(PO_4)_2 + 4OH^- \text{ at pH 8.0}$ $3CoO + 2PO_4^{3-} + 3H_2O \rightleftharpoons Co_3(PO_4)_2 + 6OH^- \text{ at pH 11.0}$

- Carbon working electrode surface of Screen Printed Electrode (SPE) modified by selective combinations of Graphene Oxide, Pyrrole, Cobalt Oxide nanoparticles, Tin (IV) Chloride, Diphenyltin Dichloride, or Ammonium Molybdate by dropcasting method
- Different concentrations of KH_2PO_4 aqueous solution used to determine the sensitivity and lower detection limit (LOD) of phosphate ion (PO_4^{3-}) of the developed sensor using open circuit voltammetry



High concentration range

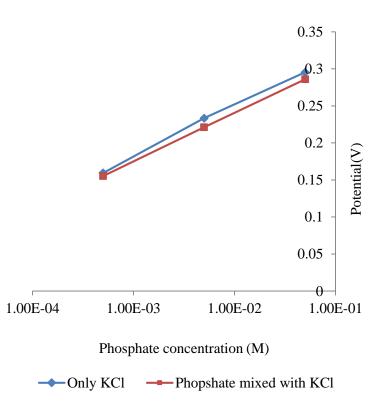
Low concentration range

0.3 0.3 0.25 0.25 $y = 0.0067 \ln(x) + 0.2784$ $R^2 = 0.9864$ 0.2 0.2 Potential (V) Potential (V) $y = 0.0229 \ln(x) + 0.5902$ $R^2 = 0.9781$ 0.15 0.15 0.1 0.1 0.05 0.05 $\mathbf{0}$ 0 1.00E-11 1.00E-10 1.00E-09 1.00E-08 1.00E-07 1.00E-09 1.00E-07 1.00E-05 1.00E-03 1.00E-01 Phosphate concentration (M) Phosphate concentration (M)

Phosphate detection using mixture of Pyrrole and Ammonium molybdate modified SPE in KH₂PO₄ aqueous solution at pH 4.5 (left)



Insignificant interference by KCI



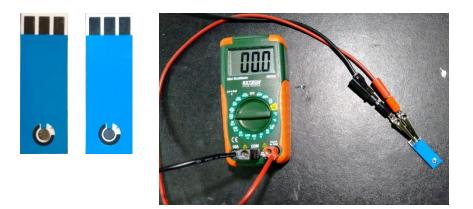
Interference test of Phosphate ions in presence of Cl⁻ ions using mixture of Pyrrole and Ammonium molybdate modified SPE in KCl solution and KCl in KH₂PO₄ aqueous solution at pH 4.5



• Our team has demonstrated a highly sensitive phosphate sensor that can be used as a simple hand-held device

In Summary

- The materials for manufacture are inexpensive and easy to obtain
- Extensive training will not be necessary to use the device
- Licensees can derive further profit from the use of one time disposable sensors







Next Steps

- Determine whether sensors can be used in longer term applications or continuous use:
 - Sensor will be submerged in standard solution for certain period of time, and then use it for the measurements to characterize the sensitivity change over time and robustness
- Test sensors further to characterize effect of temperature (5°C-50° C) on detection, as well as appropriate temperature range for the detection
 - The sensor will be tested in pressure chamber with pressure up to 80 psi (the pressure regulator in residential use is set between 40-50 psi)
- Find partner to manufacture and develop the final prototypes



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