Development of Analytical Methods for Determination of Nitrite and Nitrate in Plasma Activated Solution

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Nitrite and Nitrate (NO_2^- and NO_3^-)

- Nitrite is a nitrogen oxoanion that is formed when nitrous acid is deprotonated. As nitrite is a metabolic end product for nitric oxide (NO), which is increased during inflammation; nitrite levels can be used to assess NO production and thus inflammation.

- Nitrate is a nitrogen oxoanion formed by loss of a proton from nitric acid. Principal species present at pH 7.3. It is a nitrogen oxoanion, a member of reactive nitrogen species and a monovalent inorganic anion. It is a conjugate base of a nitric acid.

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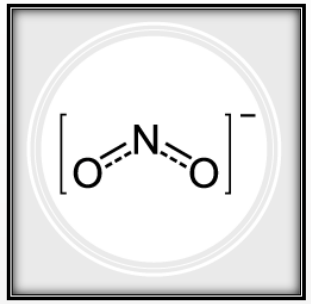
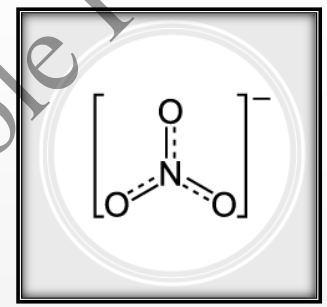
Difference Between Nitrite and Nitrate





Nitrite	Nitrate
Made up of a nitrogen atom and two oxygen atoms	Made up of a nitrogen atom and three oxygen atoms
The oxidation number of nitrogen in nitrites is +3	The oxidation number of nitrogen in nitrates is +5
Forms a weak acid known as nitrous acid	Forms a strong acid known as nitric acid
Has a bent molecular geometry shape	Has a trigonal planar geometry shape
Oxidized to form nitrates	Reduced to form nitrites
Used in food preservatives	Used in fertilizers and explosives

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Sources of Nitrite and Nitrate

- Wastewater and Septic System Effluent
- Fertilizer Runoff
- Pesticides
- Industrial Discharge
- Inorganic and organic compounds

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Risk for health

- Nitrite reacts with hemoglobin in human blood to produce methemoglobin, which limits the ability of red blood cells to carry oxygen. This condition is called methemoglobinemia or "blue baby" syndrome (because the nose and tips of ears can appear blue from lack of oxygen).

- High nitrate and nitrite levels can also cause methemoglobinemia in livestock and other animals.

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Impact on organisms in the water

- High concentrations of nitrate and/or nitrite can produce "brown blood disease" in fish.
- Brown blood cannot carry sufficient amounts of oxygen, and affected fish can suffocate despite adequate oxygen concentration in the water.
- If excessive amounts of nitrites and nitrates are added to the water, algae and aquatic plants can be produced in large quantities. When these algae die, bacteria decompose them, and use up oxygen. This process is called Eutrophication.

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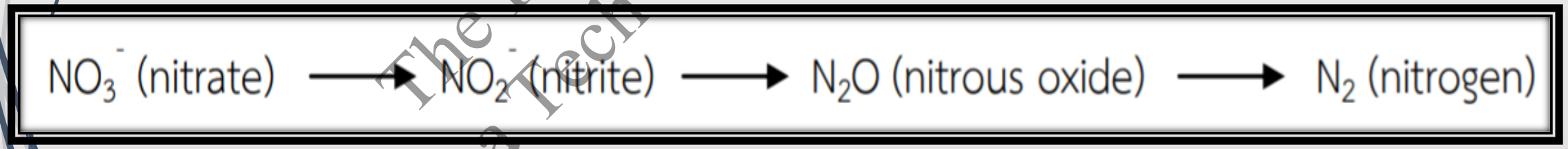
Reaction

Nitrification

Denitrification



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Flow Injection Analysis (FIA)

- The first definition, given by Ruzicka and Hansen 1975 was "A method based on injection of a liquid sample into a moving un segmented continuous stream of a suitable liquid. The injected sample forms a zone, which is then transported toward a detector''

- The analysis of the Flow injection depends on several factors, including
  - injection of samples
  - dispersion
  - the time necessary for reaction and to record events in each cycle

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The principle of FIA

- The idea of FIA is a based on three factors: the **first** factor is the reproduction process for the volume of the sample injection, the **second** factor is the control of sample dispersion and the **last factor** is the replication time of the injected sample via the flow system.

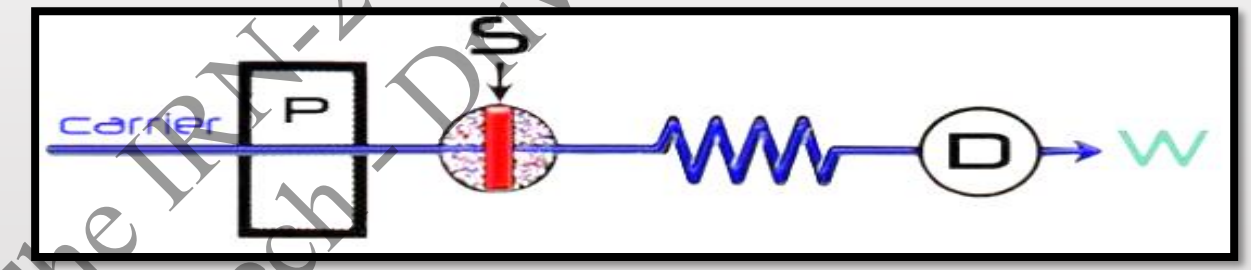

Fig.1: A single-line FI manifold; P: pump; C: carrier stream, S: sample injector, RC: reaction coil, D: detector and W: waste

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Application of FIA

- Pharmaceutical application
- Environmental analysis; sea water, waste water, sediments
- Food analysis; fruit juice, soft drinks, wine , milk and dairy products
- Biological material; Plants, animals
- Mineral material; soil, fertilizers, alloys

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Objectives

- To develop flow analysis method for determining nitrite and nitrate

- To apply to plasma activated water

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Experiment

- Sample solution was injected into a flow injection system and flowed to mix with sulfanilamide (SAM) in phosphoric acid (H_3PO_4) solution in a mixing coil no.1 to form diazonium salt. It was further reacted with N-(1-Naphthyl) ethylenediamine dihydrochloride solution (NED) in a mixing coil no.2 resulted in a pink solution, which was detected the color intensity by using a homemade LED/LDR colorimeter.

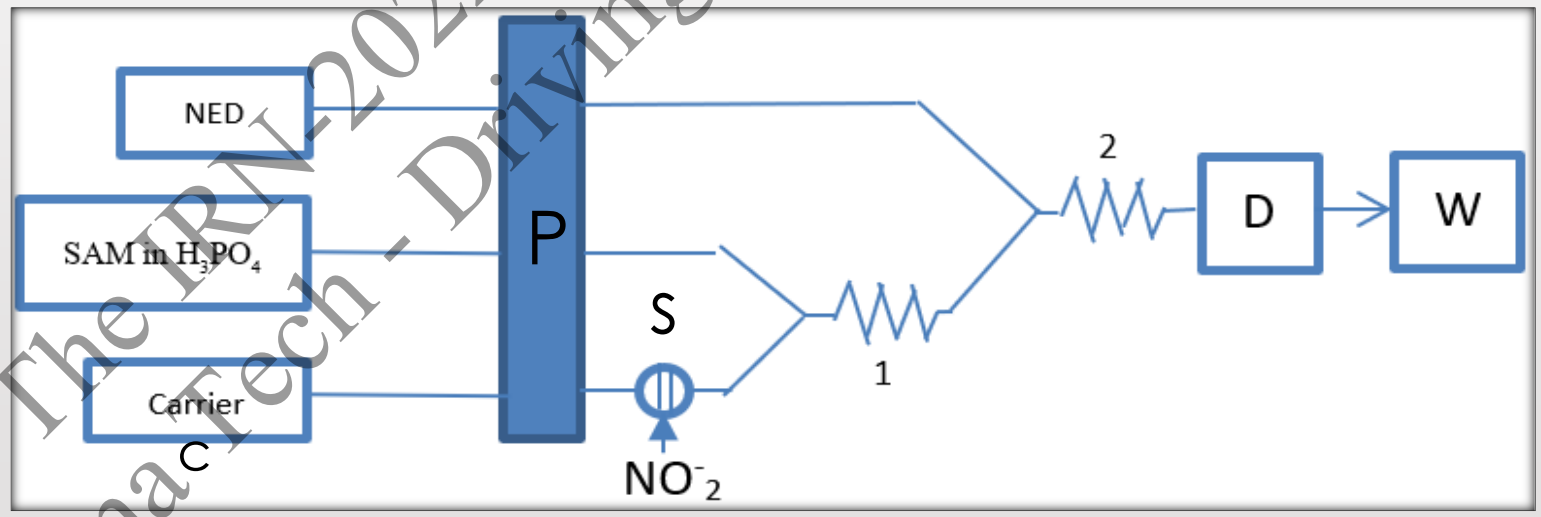

Fig.2: FI manifold of nitrite; P: pump; C: carrier stream, S: sample injector, 1: mixing coil, 2: mixing coil, D: detector and W: waste

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Griess Reaction

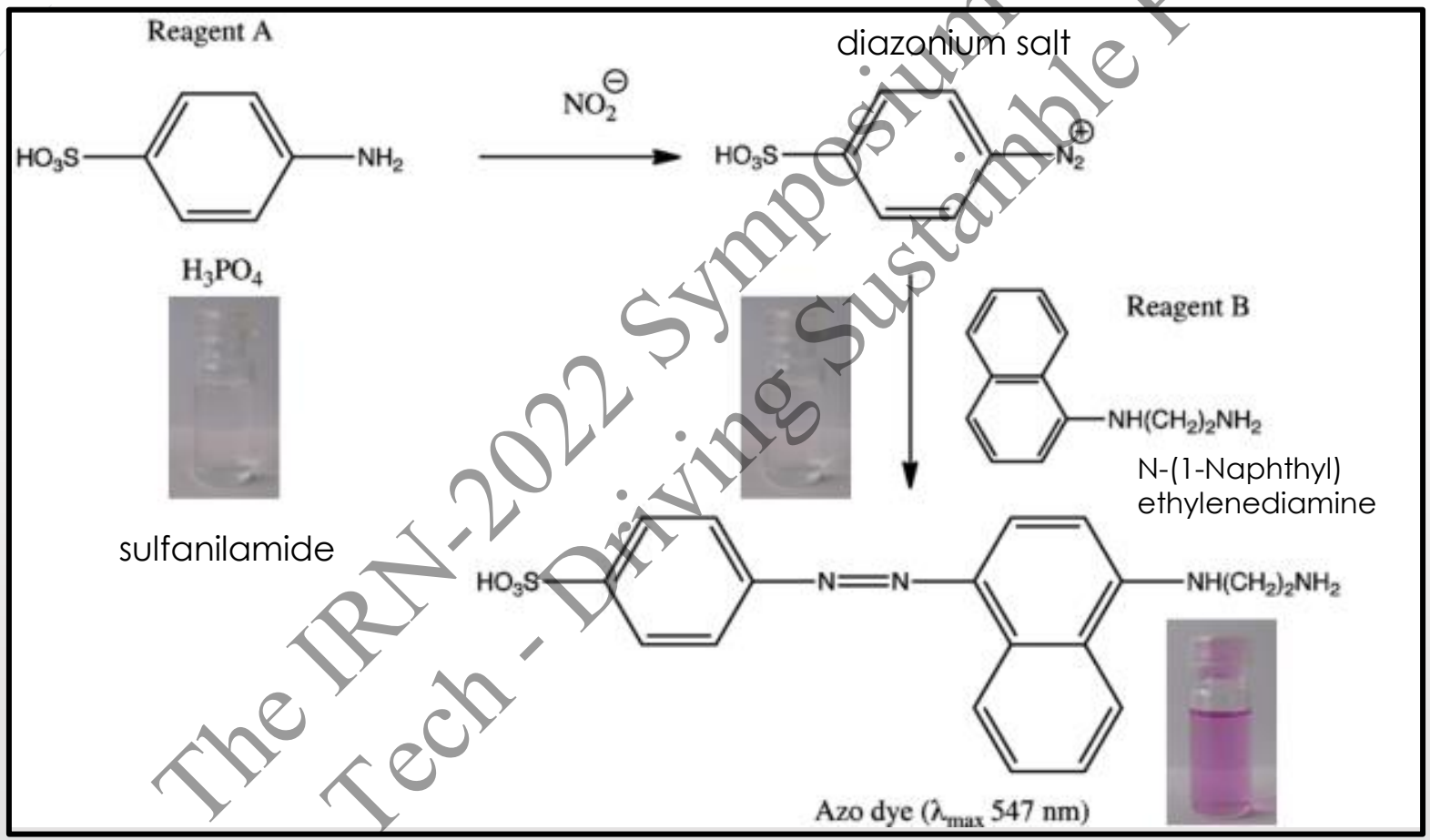

Fig. 3: Griess reaction for nitrite analysis in the experiment

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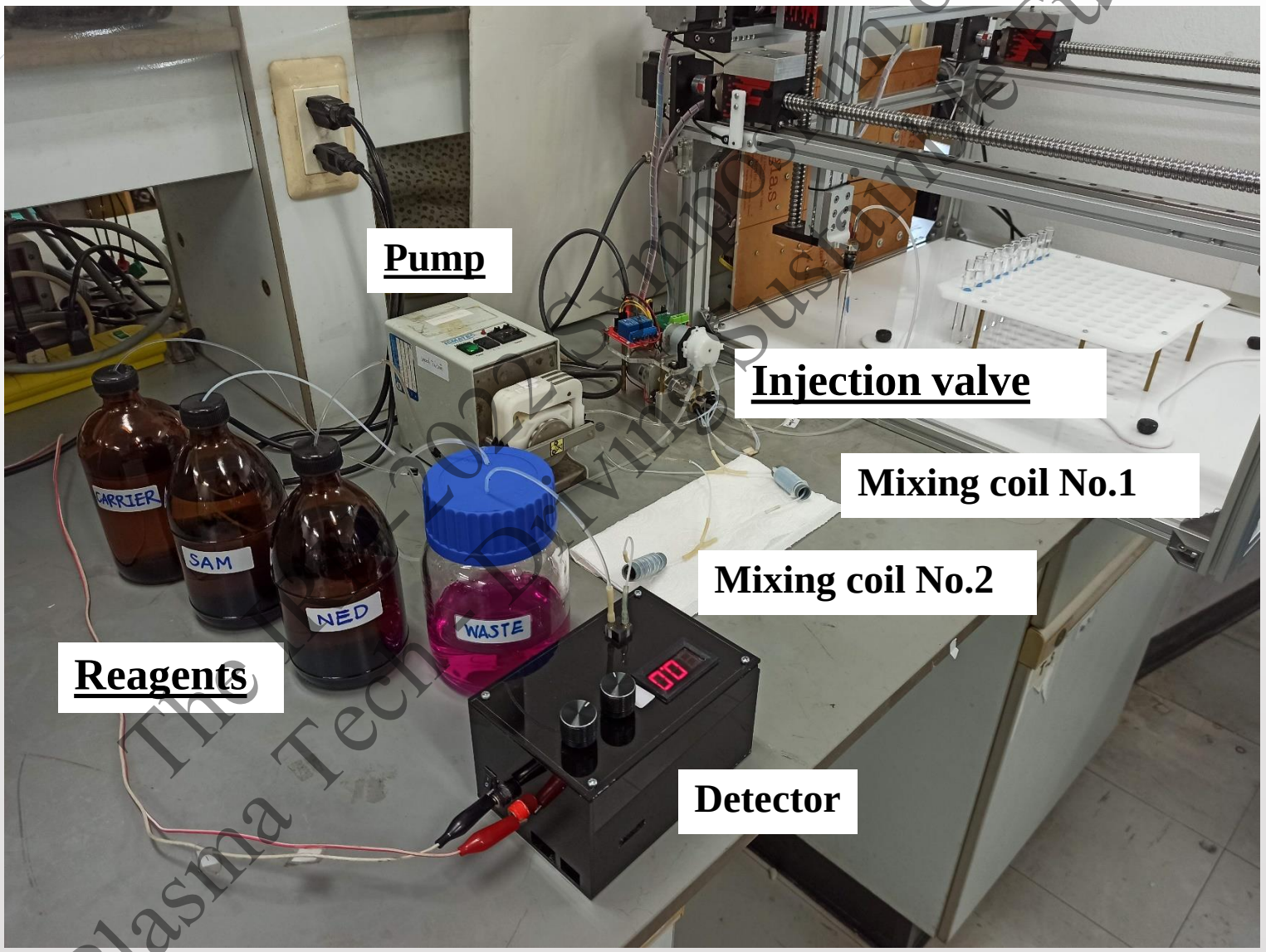
Instruments and Reagents



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Process (video)

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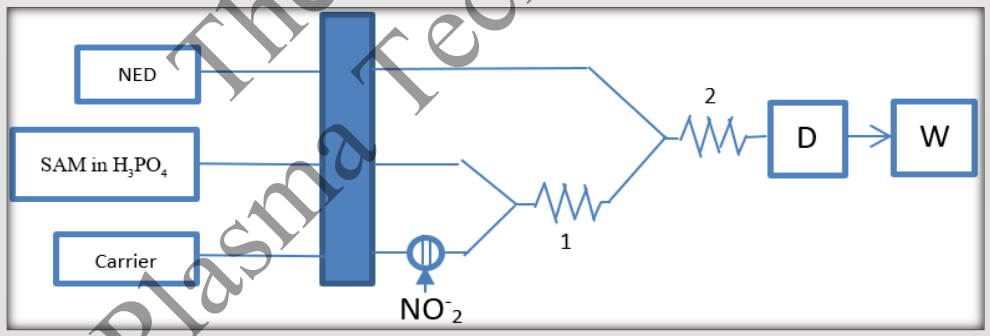
Condition

Concentration of Sulfanilamide in 10% Phosphoric acid (mM)	2.0
Concentration of N-(1-Naphthyl) ethylenediamine dihydrochloride (mM)	1.0
Injection volume (μL)	200
Length of mixing coil No.1 (cm)	100
Length of mixing coil No.2 (cm)	100
Flow rate (mL/min)	2.6



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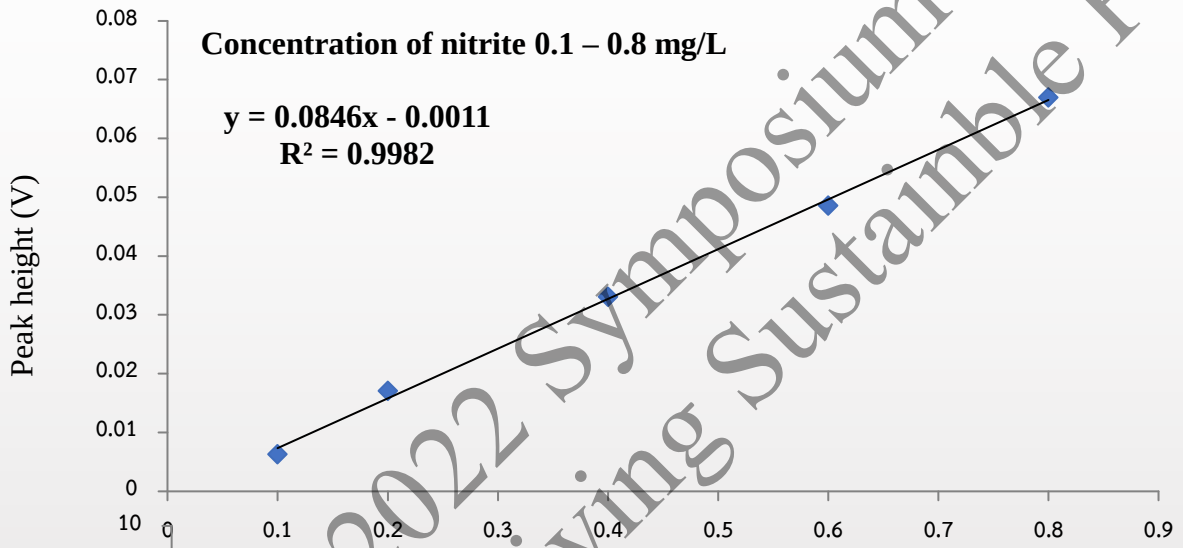
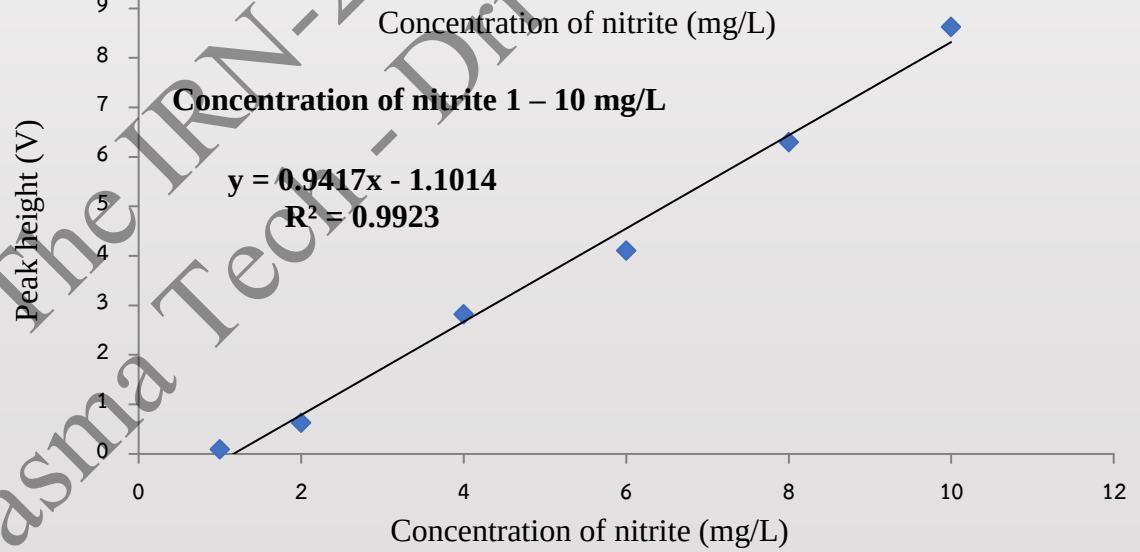
Calibration curve





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FIA Gram

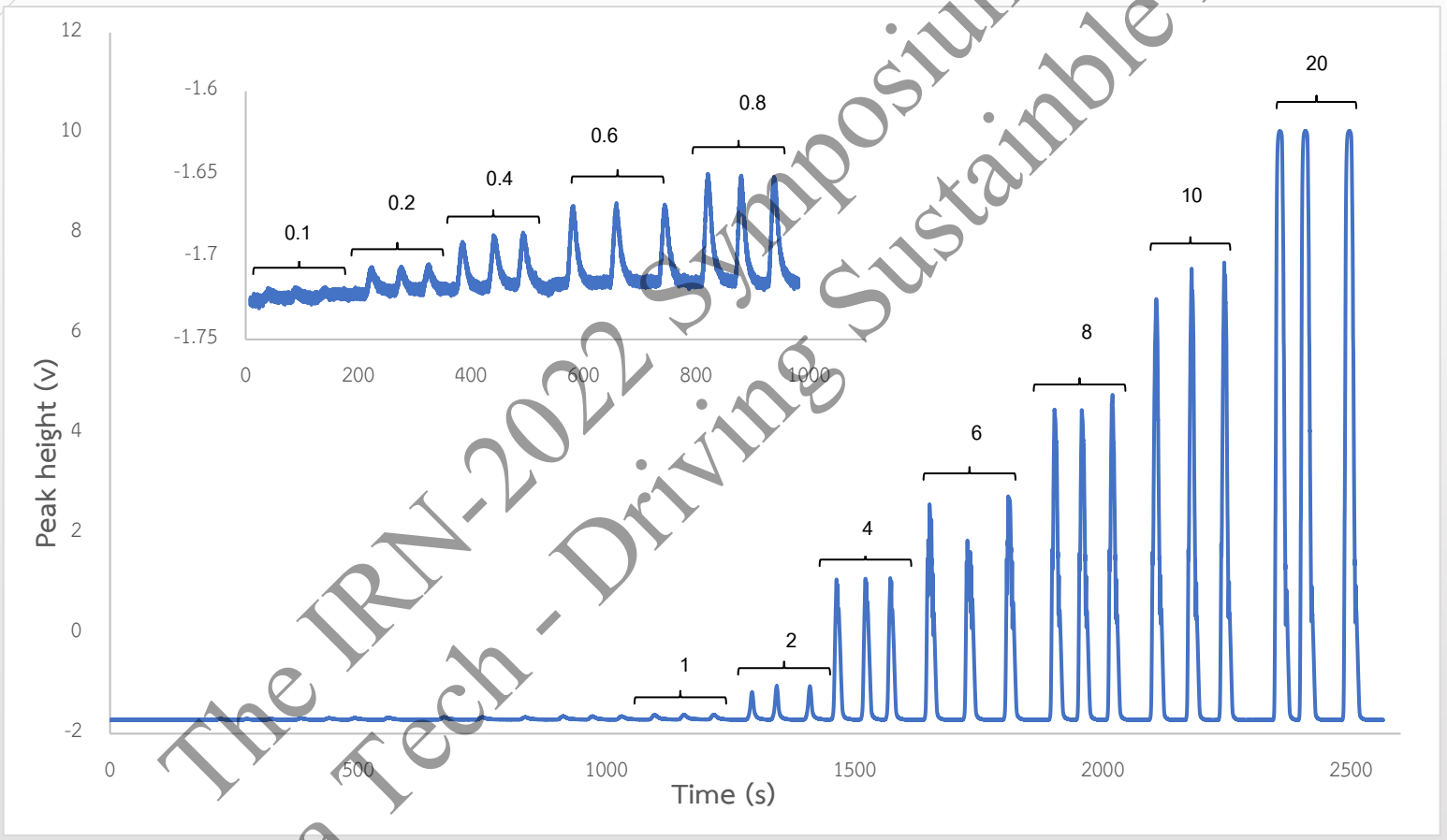

Fig.4: FIA Gram of standard nitrite (mg/L)

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Conclusion

- The calibration graphs were constructed by plotting between peak height and nitrite concentration, which were linear in the range of 0.1-0.8 mg/L and 1-10 mg/L.

- Limit of detection (LOD) and limit of quantitation (LOQ) were 0.08 and 0.13 mg/L, respectively.

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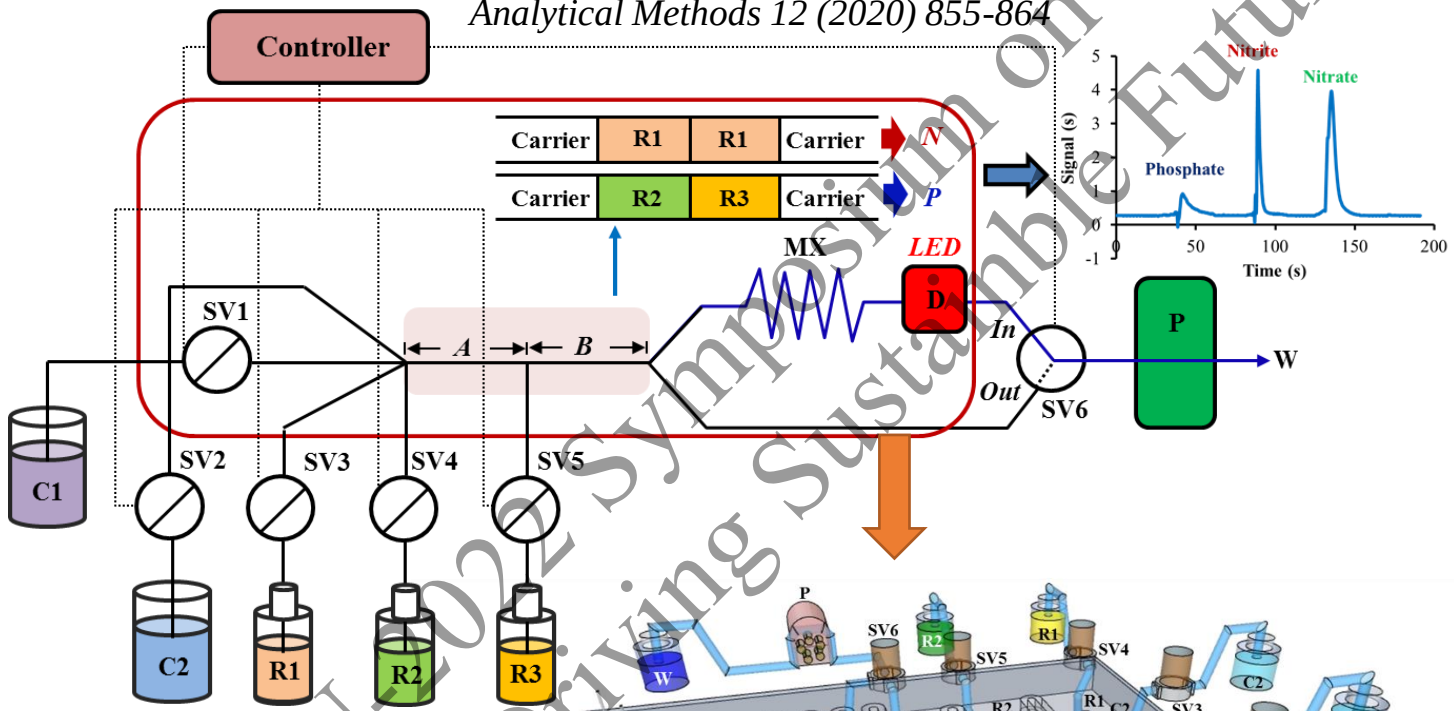
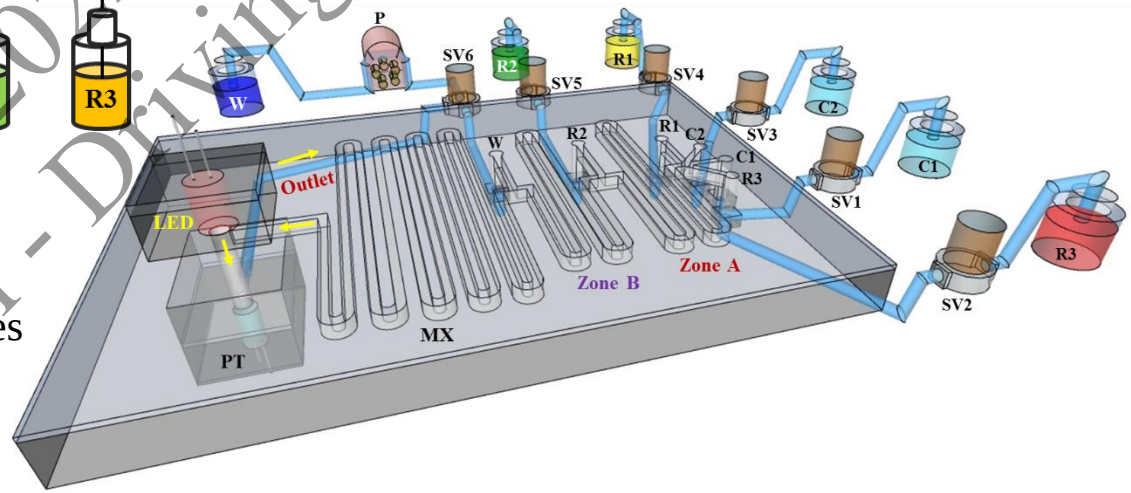
A compact multi-parameter detection system based on hydrodynamic sequential injection for sensitive determination of phosphate, nitrite, and nitrate in water samples

Wanpen Khongpet

Analytical Methods 12 (2020) 855-864





Highlights:

- Low cost compact system
- Low reagent consumption
- High sensitivity
- Consecutive analysis of multiple analytes
- Excellent choice for water quality monitoring

Analytical characteristics

- Linearity range: 0.01-0.1 and 0.3-1.0 mg of PO_4^{3-} P L^{-1}, 0.005-0.05 mg of NO_2^- N L^{-1}
  0.01-0.12 mg of NO_3^- N L^{-1}
- LOD: 0.005 mg of PO_4^{3-} P L^{-1}, 0.0026 mg of NO_2^- N L^{-1}, 0.005 mg of NO_3^- N L^{-1}

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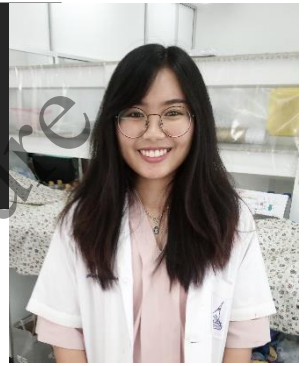
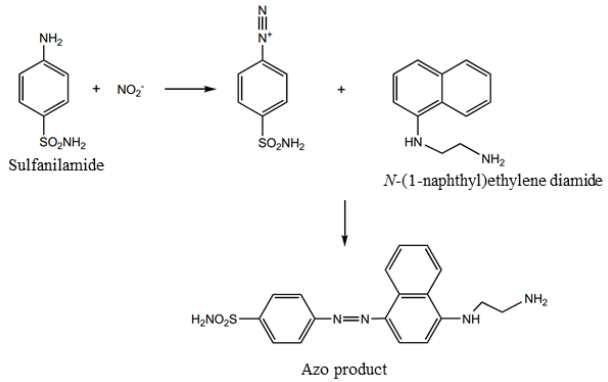
Development of a Compact Smartphone-based Analyzer for Colorimetric Determination of Nitrite and Phosphate



Chidkamon Thunkhamrak

Determination of nitrite



Determination of phosphate

$$PO_4^{3-} + 12MoO_4^{2-} + 27H^+ \rightarrow H_3PO_4(MoO_3)_{12} + 12H_2O$$

$$H_3PMo(VI)_{12}O_{40} + \text{Reductant} \rightarrow [H_4PMo(VI)_8Mo(V)_4O_{40}]^{3-}$$

Determination of nitrite

* **Linear range : 0.2-2.0 and 2.0-50.0 mg L^{-1}**
* **LOD : 0.1 mg L^{-1}**

Determination of phosphate

* **Linear range : 0.25-10 mg L^{-1}**
* **LOD : 0.24 mg L^{-1}**

Highlights

* **Convenient**
* **Fast**
* **Inexpensive device for colorimetric analysis**

Smartphone-based analyzer

The step for determination of nitrite and phosphate by smartphone-based analyzer.

Sample	Nitrite (mg L^{-1})		Phosphate (mg L^{-1})	
	UV-Visible Spectrophotometry	Developed analyzer	UV-Visible Spectrophotometry	Developed analyzer
1	2.41±0.09	2.53±0.56	3.05±0.36	2.97±0.14
2	1.58±0.08	1.60±0.32	0.84±0.11	0.80±0.16
3	2.05±0.16	2.35±0.65	2.40±0.33	2.21±0.22

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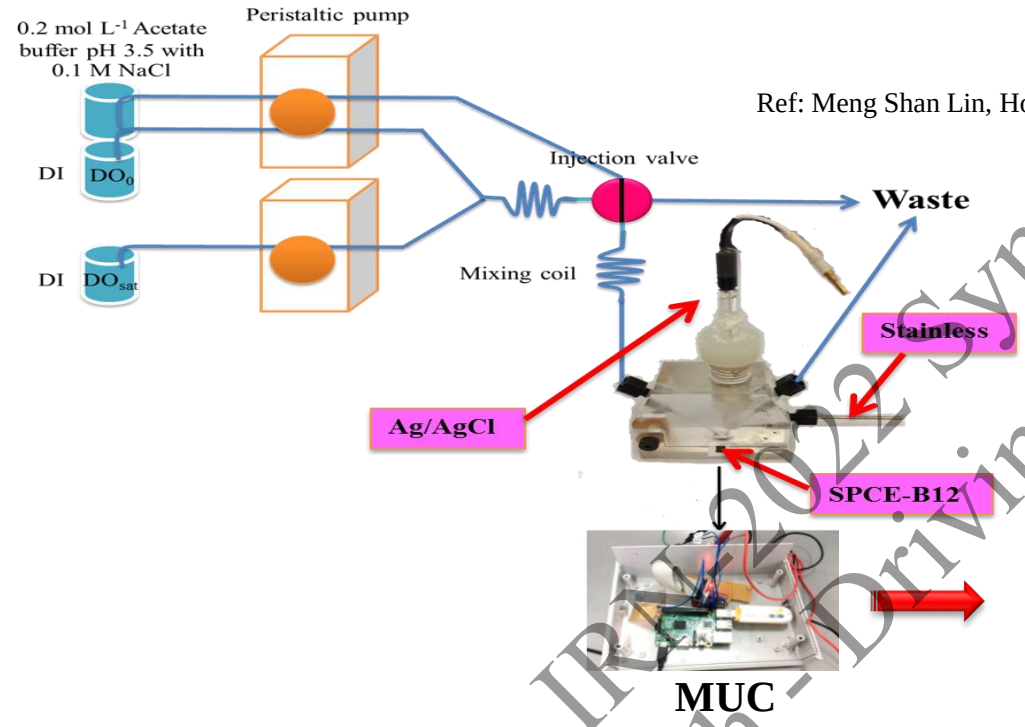
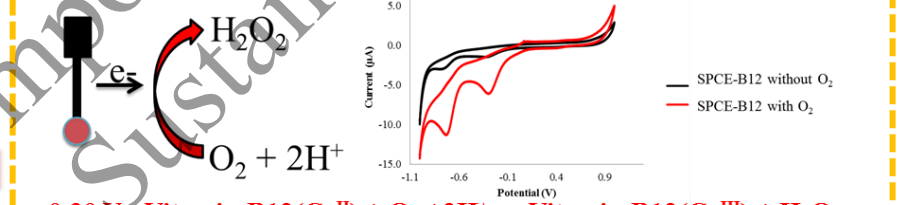
Programmable flow injection amperometric system for remote monitoring of dissolved oxygen in water

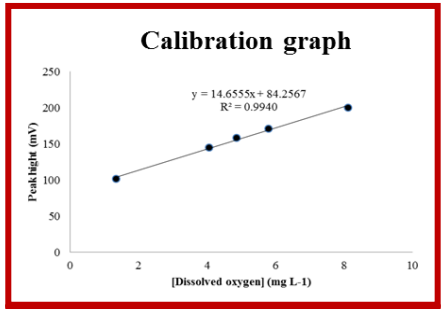
Natcha Kaewwonglom

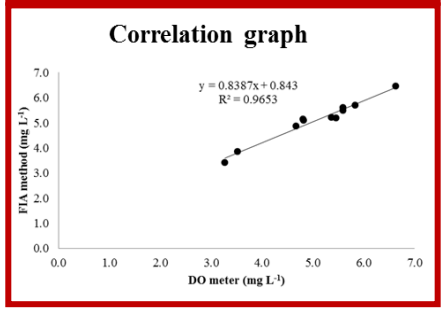
Ref: Meng Shan Lin, Hoang Jyh Leu, Chien Hung Lai, Analytica Chimica Acta 561 (2006) 164–170





- 0.30 V : Vitamin B12(Co^{II}) + O_2 +$2H^+$ → Vitamin B12(Co^{III}) + H_2O_2
- 0.67 V : Vitamin B12(Co^{II}) + H_2O_2 +$2H^+$ → Vitamin B12(Co^{III}) + $2H_2O$





Advantages

- Short time to analyze
- Low cost instruments
- Simple operation
- Easy monitoring
- Membrane-free, maintenance-free
- Can monitoring at a certain period

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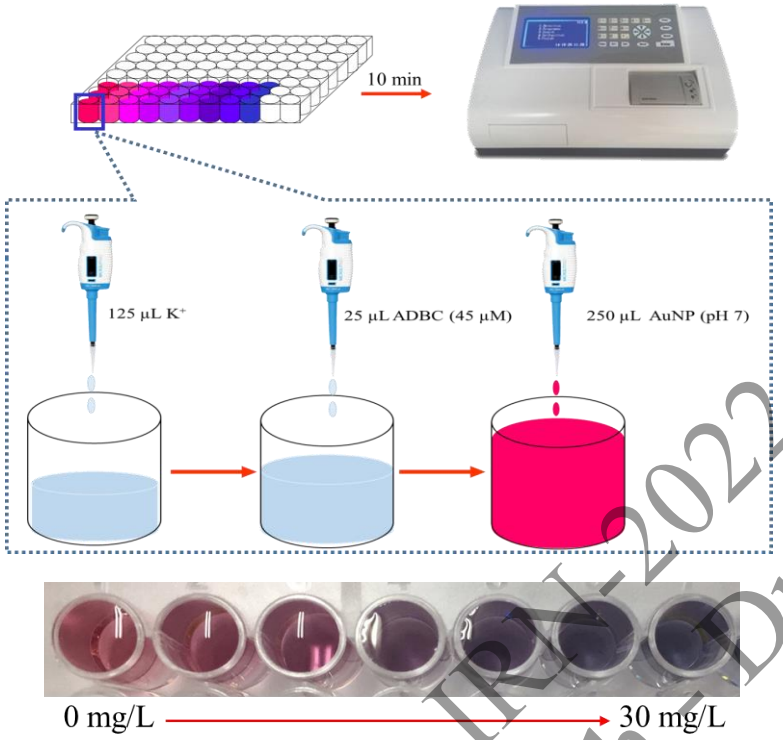
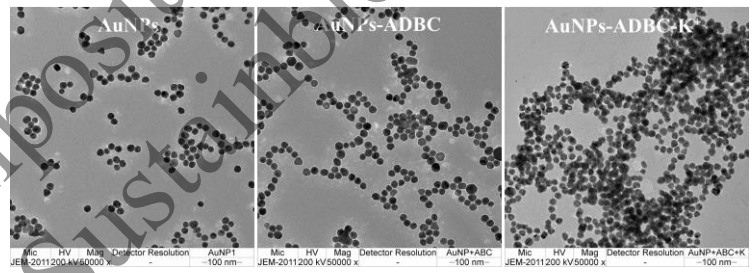
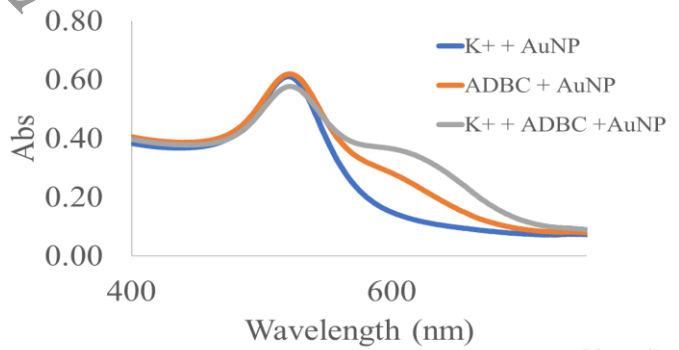
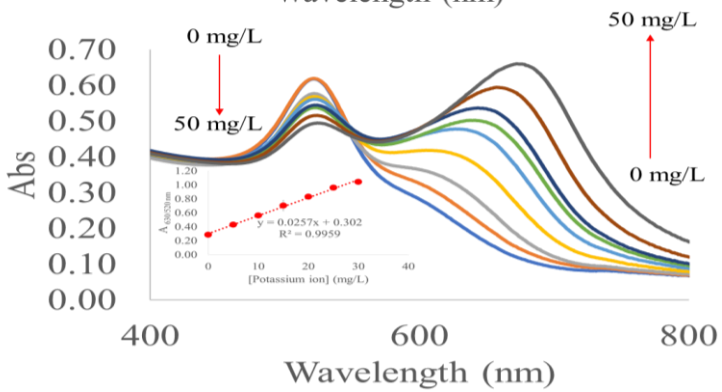
Alternative Colorimetric Gold-Nanoparticle Aggregation Sensor for Potassium Ion Detection in Soil Using 4'-Aminodibenzo-18-crown-6

Natcha Kaewwonglom









Advantages

- ✓ An alternative colorimetric sensor for K^+ detection
- ✓ A simple for operation rapid and easy for detection with naked eyes

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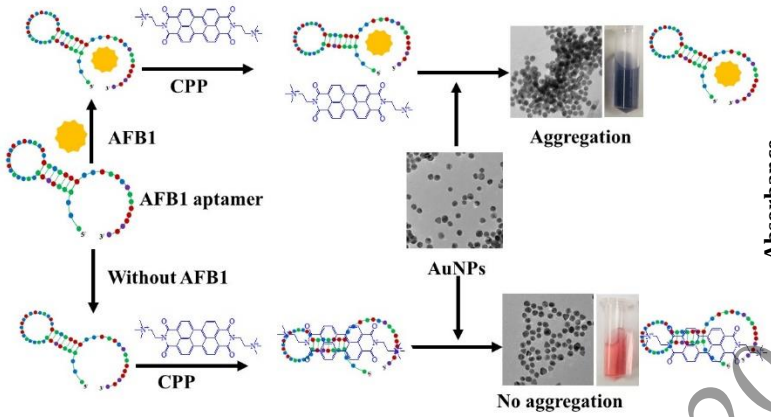
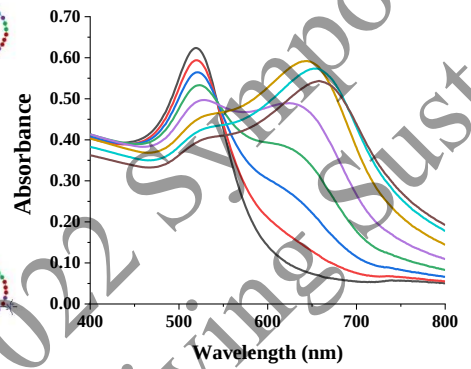
Label-Free Colorimetric Aptasensor for Rapid Detection of Aflatoxin B1 by Utilizing Cationic Perylene Probe and Localized Surface Plasmon Resonance of Gold Nanoparticles

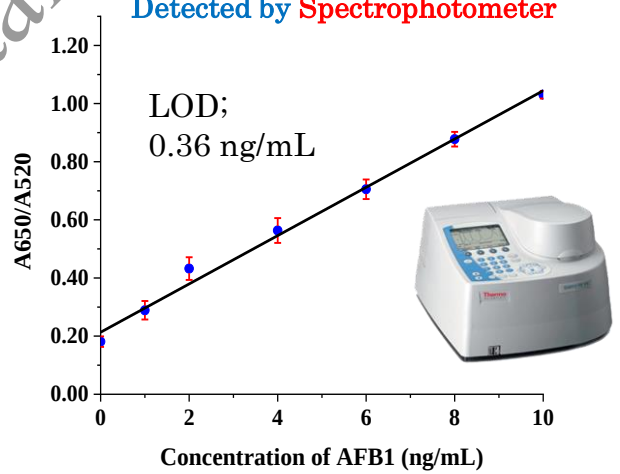
SCHEMATIC PRINCIPLE OF THE COLORIMETRIC APTASENSOR

Sensors & Actuators: B. Chemical 320 (2020)





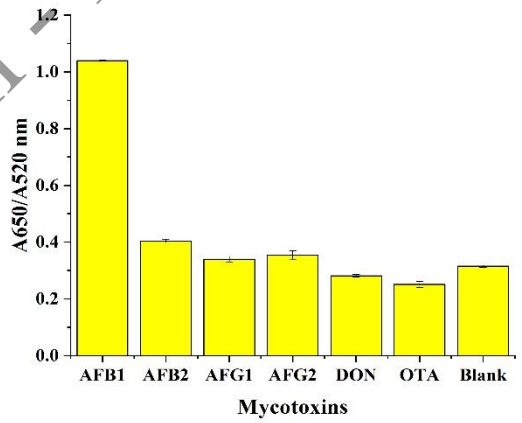
Detected by Spectrophotometer



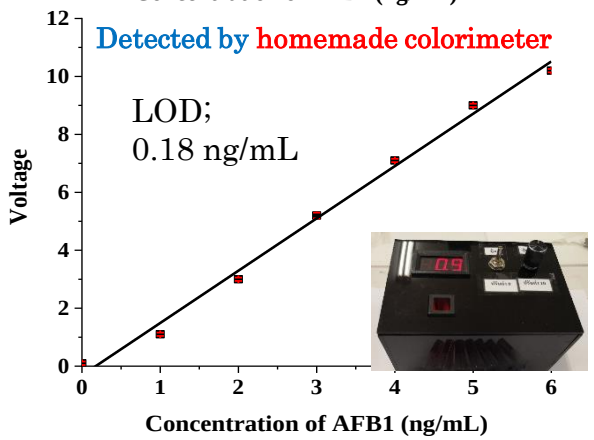
Highlights

- Cationic perylene probe was synthesized to be an inducer of AuNPs aggregation.
- A label-free colorimetric aptasensor based on localized SPR of AuNPs for rapid detection of AFB1 was presented.
- The proposed method provides simplicity, visualized detection, and portability.
- Linearity and sensitivity of the developed method are practical for real sample analysis with high accuracy and precision.

Interferences



Detected by homemade colorimeter



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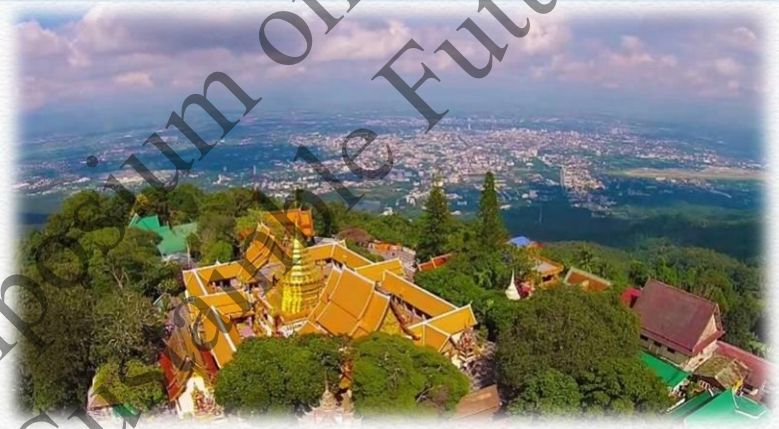
THANK YOU FOR YOUR ATTENTION !



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