

# Development and Testing of an Electrochemical Sensor for Detection of Nitrate in Water

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## ABSTRACT

Monitoring of water quality is paramount due to several environmental issues. Contemporary measurement methods for contaminant quantification are expensive, laboratory-based and time-consuming. Hence, developing a low-cost, convenient sensing system is appropriate. An electrochemical impedance spectroscopy-based nitrate sensing system has been developed. The system measures the nitrate concentration in water is stand-alone, robust, real-time and low-cost. The microcontroller in the system generates the excitation signal applied to the sensor for data processing and controlling time interval for the switch. The calibration samples were prepared by the serial dilution of a nitrate stock solution using sodium and ammonium nitrate with different concentrations. The sensor was immersed in the solution to observe the impedance change at various nitrate concentrations. The experimental results showed a good linear relationship between the concentration and real part of the measured impedance. The computational model for nitrate concentration was predicted based on the experimental results. The sensor was also tested in the water samples collected from different sources, and the results were validated with the applied laboratory testing results using contemporary techniques. The experimental results showed that the sensing system is more sensitive to the lower nitrate concentrations in the water.

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## Introduction

In our planet, the water resource makes up 97% from the ocean and 3% from freshwater. Most of the freshwater (around 69%) is stored in the icecaps and glaciers, and there is only about 30% of total freshwater (around 1% of total water source) [1] found in the groundwater and surface water. Most freshwater comes from rainfall and snow which are dissolved from the atmosphere and flow into the sea or is absorbed by land or evaporates back in to the atmosphere. Moreover, freshwater extracted from rivers, lakes and ground are used for agriculture (70%), industrial processes (22%) and domestic use (8%) [2]. Freshwater is an essential natural resource which is necessary for all living organisms because it supplies drinking water and provides food and habitat. Freshwater also supports human recreational activities such as swimming, fishing and boating. Therefore, clean water is a key issue not only for human and animal health, but also the health of aquatic organisms.

The degree of urbanization has grown exponentially in the last few decades. This has resulted in a rapid increase of contamination in the water sources. One of the most important of these contaminants is the nitrate salt. Nitrate-nitrogen (NO<sub>3</sub>-N) is one of an essential element for the growth of all plants and animals in water as it is an important component for the supply of protein [3, 4]. It is also used in the agricultural sector to increase plant and therefore animal production. However, nitrate can become a contaminant if the concentration in the water rises above a certain threshold concentration, a common problem in surface and groundwater draining the

agricultural areas all over the world [5] in most urban areas, the NO<sub>3</sub>-N concentrations in groundwater are commonly higher than the threshold concentration in the agricultural areas,

The increase in nitrate concentration in groundwater arises mainly from natural and anthropogenic sources. However extensive areas in some parts of the world have increasingly nitrate concentration due to natural leaching the nitrate accumulation under environmental conditions [6]. Nitrate (NO<sub>3</sub>) is an important and commonly occurring nitrogen species in the environment. It is applied in both urban and rural areas as a component of fertilizer, and is a major component of concern in the effluent of wastewater treatment plants. Excess nitrate in freshwater and marine ecosystems can lead to algal blooms and eutrophication. When ingested, nitrate is known to be reduced to nitrite which is further converted to N-nitrosamines, which are suspected carcinogens. A specific toxic effect of nitrates on infants is called methemoglobinemia, a condition that can result in mental retardation, or even death.

Due to its role in ecosystem dynamics, and its potential impact on human health, nitrate levels in water are regulated and carefully monitored in engineered and environmental systems. For example, drinking water from groundwater wells in agricultural regions must be regularly checked for nitrate. There are many methods for measuring aqueous nitrate concentrations, including spectroscopic [7, 8], chromatographic [9] and electrochemical [10, 11] techniques. Such methods often require expensive equipment, and/or require extensive pre-treatment procedures which may involve the use of other toxic chemicals.

A rapidly developing technique for the rapid determination of the concentration of nitrate other ionic species involves the use of ion selective electrodes (ISE). Despite the promising nature of this technology, many early ISE were found to be insufficiently selective and sensitive for environmental applications. It has recently been shown that Electrochemical Impedance Spectroscopy (EIS) is a method that can be used to determine the concentration of nitrate in water.

Through the importance of nitrate detection and the limitations of the current measurement options, the motivation of this project is to develop a sensing system which can be portable, suitable for in-situ measurement with a low cost for accurate nitrate detection in water. Considering the disadvantages of the current methodologies for detecting nitrate, this project aims to develop a sensing system based on the electrochemical impedance spectroscopy method. The objectives of the work are to investigate the characterization of the impedance of the sensor in variable nitrate concentration, calibrate the impedance of the sensor to detect nitrate concentration, develop a low-cost and in-situ sensing system, and evaluate the developed system by comparing it with the common laboratory system

Electrochemical Impedance Spectroscopy (EIS) is a method to determine the current response of an electrochemical cell by applying a small sinusoidal signal. EIS method is widely used in various applications such as detection of bacterial endotoxin in food [12], determination of the corrosive behaviour of materials [13, 14], analysis of electrical properties for controlling soymilk coagulation process [15], evaluation of impedance response to the Phthalate concentration [16] and other bio-sensing applications [17]. In EIS method, a periodic sinusoidal voltage is applied to the sensor, so there is a phase shift between the applied voltage and current flow through the sensor. Therefore, the total impedance can be divided into the real part and the imaginary part.

The Randles equivalent circuit is the mostly used to express EIS evaluation in electrical model form. Randles equivalent circuit consists of series resistance  $R_e$ , the parallel combination of double layer capacitance  $C_{dl}$  and charge transfer impedance  $Z_w$  and charge transfer resistance  $R_t$  [18] shown in figure 1, where  $R_e$  = Series resistance,  $C_{dl}$  = Double layer capacitance,  $R_t$  = Charge transfer resistance and  $Z_w$  = Charge transfer impedance. The Nyquist plot for Randles circuit without  $Z_w$  is semi-circle but there is diffusion on the semi-circle when  $Z_w$  is added. This happens when the electrode is covered with other coatings, so the electrochemical reaction is influenced.

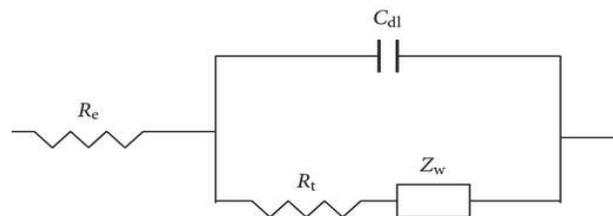


Figure 1. Randles equivalent circuit

The techniques for the detection of nitrate are either simultaneously or sequentially. Simultaneous technique means the detection is independent of other analytes in one measurement such as capillary electrophoresis [19, 20] and electrochemical [21, 22]. Electrochemical detection is based on the evaluation of potential, current or charge to characterize an analyte's chemical reaction or determine its concentration. Zn (II), the complex-based coating on polymeric membranes, was developed to determine the nitrate concentration range from  $5.0 \times 10^{-5}$  to  $1.0 \times 10^{-1}$  M. This developed system based on the potentiometric sensor showed a fast response time of fewer than 25 seconds and an excellent detection limit of around  $10^{-5}$  M [21]. Another potentiometric nitrate sensor was developed by [23]. This sensor consists of an all-solid-state nitrate selective electrode with lipophilic carbon nanotubes and a miniaturized reference electrode. It has the detecting limit of  $5 \times 10^{-7}$  M with the response time of 5 seconds. The amperometric method is used to measure the current at a given electrode to analyze the response of analyte as the current is changing with varying of concentration. Reference [24] developed the electrochemical sensor to detect nitrate based on the Cellulose Acetate membrane. A three-electrode electrochemical sensor was designed based on nitrate-selective polypyrrole (Ppy) as working electrode [25, 26]. The working principles of this system are that a large number of nanopores will be produced on the surface of the Ppy nanofiber when the working electrode is doping into the nitrate solution. The nitrate detection can be achieved by charge distribution within doped Ppy nanofibers [25]. Similarly, the nitrate was detected by using doped Ppy nanowires integrated with microfluidics [26].

The voltammetric method is also used to detect the nitrate concentration at a copper electrode [27, 28] without reagent electrodes. Based on the deposition of macro porous structure, the copper deposit showed selectivity for the nitrate ion with the detection range of 10 to 200  $\mu$ M. Reference [21] researched on nitrate sensor using silver nanoparticles embedded with polymethacrylic acid matrix electrode. The detection range is linear from 0-20 mM with limit of 0.5 mM by the voltammetric sensor. In [28], an in-situ copper plated boron-doped

diamond microelectrode array was developed to detect nitrate with a limit of 0.76  $\mu$ M.

Table 1 summarizes the electrochemical detection based on methods like potentiometric, amperometric and voltammetric. Some of the advantages of electrochemical detection include simplicity and cost effectiveness, suitability for in-situ measurement, fast response and wide detection limit on the other side. The disadvantages include the sensitivity relies on the working electrode, it requires prepared reagent solutions and interference with other ions like phosphate, sulphate, chloride, etc. in the water.

Table 1. Electrochemical detection summary

Working Method	Working Electrode	Detection Limit	Reference
Potentiometric	Zn (II)	$1 \times 10^{-5}$ M	[23]
Potentiometric	Lipophilic Carbon Nanotubes	$5 \times 10^{-7}$ M	[24]
Amperometric	Cellulose Acetate	$1 \times 10^{-6}$ M	[25]
Amperometric	Ppy nanofibres	$1 \times 10^{-4}$ M	[26]
Amperometric	Ppy nanowires	$4.5 \times 10^{-5}$ M	[27]
Voltammetric	Copper	$1 \times 10^{-5}$ M	[28]
Voltammetric	Silver Nanoparticles	$5 \times 10^{-4}$ M	[30]
Voltammetric	Copper	$7.6 \times 10^{-7}$ M	[29]

### Materials and Method

The electronic circuit of the system is depicted in Figure 2 and 3. The approach used in developing the nitrate meters is simply the use of a voltage divided circuit to generate a voltage  $V_{out}$ , that is directly proportional to the concentration of nitrate, and then a microcontroller was used to measure the voltage within a given period to estimate the nitrate concentration. A voltage divided circuit was used with lm741 IC (operational amplifier) to obtain and smoothing output voltage respectively. Thus in this design, the microcontroller measure and displays the corresponding concentration of nitrate in mg/litre and display it on the LCD (Liquid crystal display) as a digital output.

The meter was calibrated to measure the concentration of nitrate in mg/litre and display them on LCD. To calibrate the system, sodium nitrate was used as sources of nitrate, standard solution was prepared from 1mg/litre of distil water ( $H_2O$ ) to 20 mg/litre there after the sensor probe was used with a standard digital meter to obtain the voltage corresponding to each concentration of the nitrate in the solution. The reading was tabulated as shown in Table 1 below. Table 1 shows that the output voltage from 1 mg/litre to 10 mg/litre was linear with a potential difference approximately 0.06 V or 60 mV. This was

used to calibrate the meter and information obtained was display on LCD as digital output.

The sensing system was developed for in-situ measurement of nitrate concentration. The developed system consists of a sensor and power supply, the signal processing circuit and control circuit, microcontroller. The functional block diagram of the system is illustrated in figure 2.

Table 2. Calibration of Nitrate meter

Milligram per litre (mg/l)	$V_{out}$ (V)	Time (sec)	Input voltage (V)
1	1.70	60	4.96
2	1.76	60	4.96
3	1.82	60	4.96
4	1.90	60	4.96
5	1.95	60	4.96
6	2.00	60	4.96
7	2.07	60	4.96
8	2.13	60	4.96
9	2.20	60	4.96
10	2.28	60	4.96
11	2.30	60	4.96
12	2.40	60	4.96
13	2.33	60	4.96
14	2.45	60	4.96
15	2.44	60	4.96
16	2.60	60	4.96
17	2.69	60	4.96
18	2.70	60	4.96
19	2.73	60	4.96
20	2.71	60	4.96

Note;

- (a) maximum reading is 10 mg/litre,
- (b) the meter must be allowed to stay inside the sample for 60 seconds,
- (c) Sensitivity of the meter is 60 mV in 1 mg/litre, and
- (d) Error  $\pm 0.04$

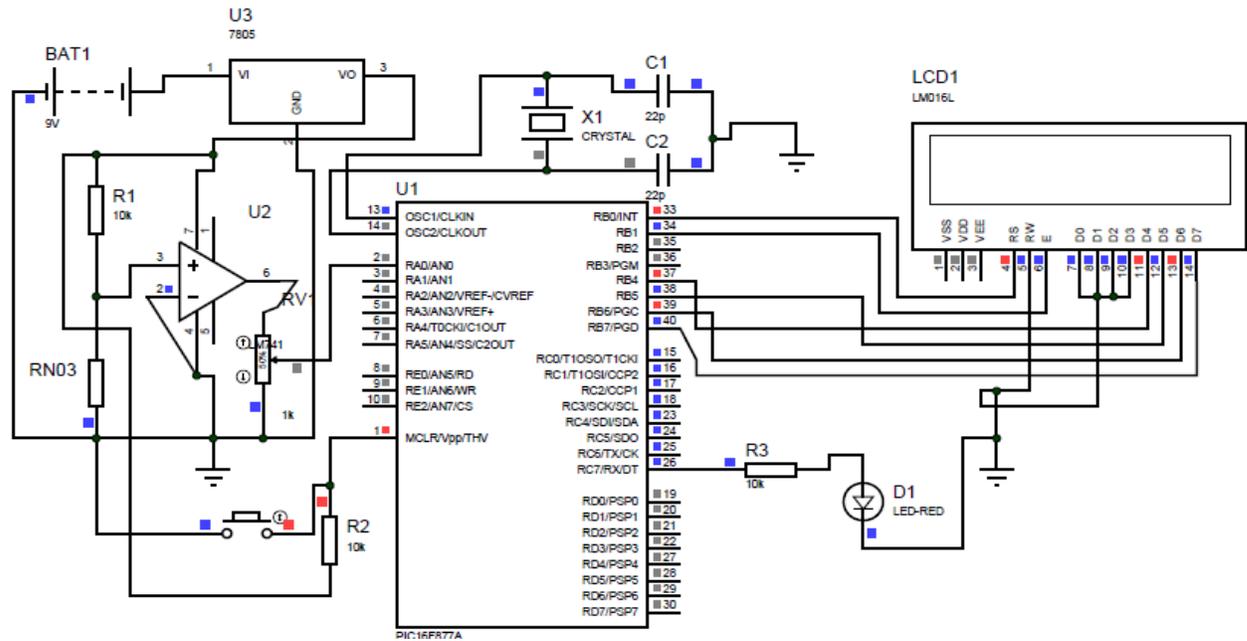


Figure 2. Circuit diagram of digital nitrate meter

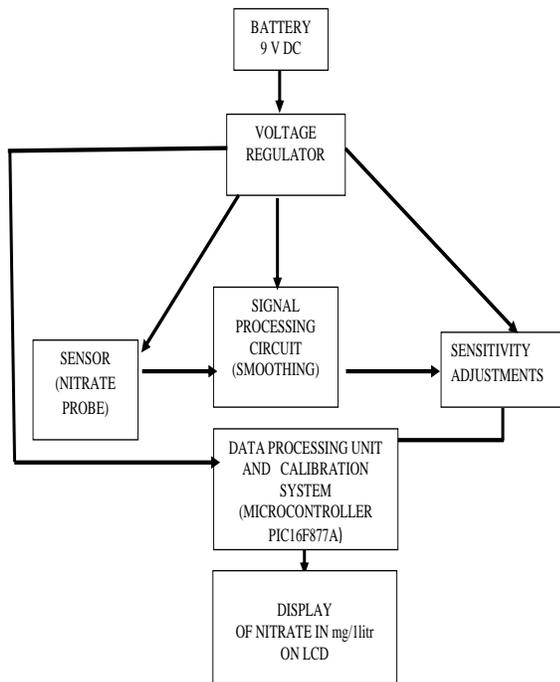


Figure 3. Block diagram of nitrate meter.

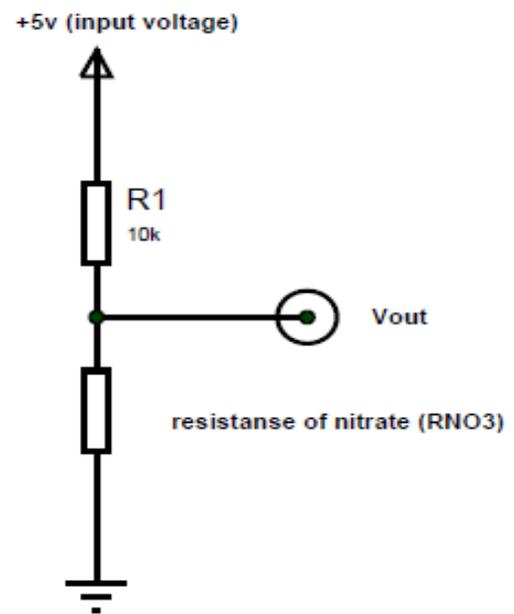


Figure 4. Nitrate sensor.

### Results and Discussion

The functional block diagram of the system is shown in figure 3. The device is a microcontroller based system with insertion sensor probe to concentration of nitrate in water.

Generally, the impedance based nitrate meters use the relationship between the resistances of nitrate to water. When the electrode of the meter is in contact with water containing nitrate and allow it to stay 60sec, there will be flow of current in the system, the output voltage in the system has a direct relationship with the resistance of the nitrate in the water. So a voltage divided rules is apply as the sensor probe as shown figure 4. The meter can be calibrated to read nitrate content mg/litre of water. All resistance nitrate meters are based on the same operating principle. The probe is inserted in the water sample the change in nitrate content causes change resistances which in turn causes change in our output voltage. This voltage measured will be smoothing with op-amp comparator (LM741 IC) to remove electrical noise from the system. This voltage is measure direct at the analog to digital converter (A/C) of microcontroller (pic16f877a). The voltage is converted back to corresponding nitrate in mg/litre and display. The basic equation relating the measured voltage ( $V_{out}$ ), which is dependent on nitrate content in water, and its resistances ( $RNO_3$ ) is given by Eq. 1.

$$V_{out} = \frac{V_{in} \times RNO_3}{R_1 + RNO_3} \quad (1)$$

where  $V_{out}$  = output voltage,  $V_{in}$  = input voltage,  $R_1$  = fixed resistance (10 kilo ohm)  $RNO_3$  = resistance of nitrate.

The nitrate sensor was tested using samples prepared at the laboratory. The nitrate sensor was tested with fifteen samples with different concentration of nitrate. For each sample the prop was immersed into the solution and allowed for about sixty seconds, after which the concentration was read up from the meter displayed, this procedure was carried out for fifteen samples and the readings were recorded as shown in Table 3. To confirm the accuracy of the nitrate sensor, it was tested alongside with conventional laboratory procedures for testing nitrate in water and the concentration of the corresponding nitrate was recorded as shown in the Table. Samples are represented by S followed by numbers.

From Table 3, it can be seen that the concentrations of nitrate in the samples as determined by the sensor were almost the same as the results obtained by the laboratory procedure for samples with lower concentration from 1 mg/l to 10 mg/l, with average difference of approximately 0.01. But the variation between the two methods for samples with higher concentration (more than 10 mg/l) were higher. For example, the difference in readings for sample S134 was 1.4. This means that this instrument can perform better when testing water with low concentration of nitrate. This is the area were improvement is recommended for this sensor. Figure 5 illustrates the correlation between results from laboratory analysis and designed system. Although there is a difference between two results, the correlation coefficient  $R^2$  is at 0.9906 which shows the potential for this new approach.

Table 3. The compared results between the designed system and laboratory measurement

Date	Sample name	Laboratory result Nitrate-N (mg/l)	Designed system result Nitrate-N (mg/l)
6/8/2016	S123	1.51	1.5
6/8/2016	S124	2.9	2.9
6/8/2016	S125	3.21	3.21
6/8/2016	S126	4.76	4.76
6/8/2016	S127	5.46	5.45
6/8/2016	S128	6.5	6.51
6/8/2016	S129	7.9	7.9
6/8/2016	S130	8.05	8
6/9/2016	S131	9.8	9.81
6/9/2016	S132	10.2	10.2
6/9/2016	S133	10.3	10.25
6/9/2016	S134	12.5	11.5
6/9/2016	S135	13.1	13.85
6/9/2016	S136	14.5	13.9
6/9/2016	S137	15	15.35

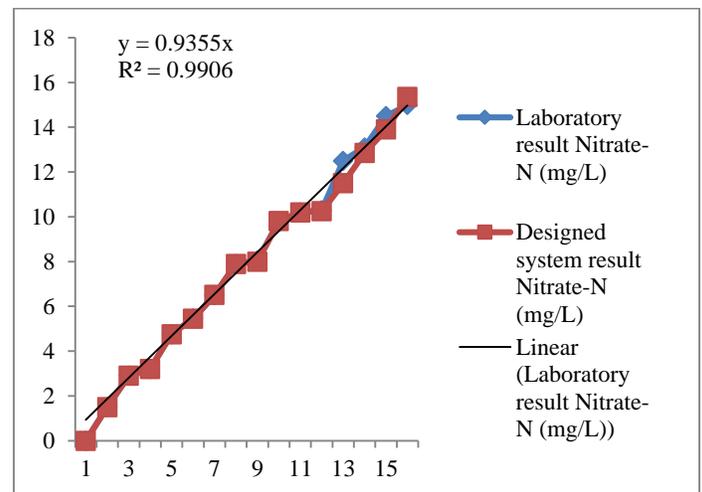


Figure 5. Comparison between laboratory method and designed system for nitration measurement

### Conclusion

This work contributed to the development of an electrochemical impedance spectroscopy based sensing system for nitrate detection by using the novel interdigital sensor. Agriculture is the primary industry for most rural population

in Nigeria and most of the nitrate contamination sources come from agricultural activities like livestock farming and fertilizer application to pasture and crops. Therefore, the nitrate level is higher than the threshold in some areas in most of these areas in Nigeria. Water quality is routinely monitored by water supply agencies in Nigeria, and water samples have to be collected manually from the field and tested in the laboratory. This requires not only expensive equipment and professional technicians but is time-consuming. More importantly, the quality of the data collected can be compromised by this approach, as water quality changes rapidly with increasing flow (i.e. storm events) and decreasing flow and monthly sampling approaches are unable to fully capture these changes. Hence, a low-cost portable/in-situ, high frequency nitrate sensor is essential to improve water quality monitoring not only in Nigeria, but for the world.

The work done includes the system characterizing of sensor impedance, testing, data collecting and analyzing. An electrochemical impedance spectroscopy based nitrate sensing system has been developed for nitrate detection. The proposed system is designed to read the nitrate concentration in water and represents a stand-alone, robust, real-time and low-cost system. The microcontroller in the designed system was used to generate the excitation signal applied to the sensor; for data processing and controlling time interval for the switch on/off. The calibration samples were prepared by the serial dilution of the nitrate stock solution using sodium nitrate ( $\text{NaNO}_3$ ) with different concentrations. The sensor was immersed in the solution to observe the impedance change at various nitrate concentration. The experimental results showed a good linear relationship between the concentration and real part of the measured impedance and the computational model for nitrate concentration was predicted based on the experimental results achieved. The sensor was also tested in the water samples with different concentrations, and the results were validated with the applied laboratory testing results. The experimental result showed that the sensing system is more sensitive to the lower nitrate concentrations in water and areas for future improvement of the system have been identified.

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