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DEVELOPMENT AND CALIBRATION OF ORP SENSOR FOR THE ESTIMATION OF MACRONUTRIENTS IN THE SOIL OF OIL PALM PLANTATION

Muhammad Yamin[1,2,*], Wan Ishak bin Wan Ismail[2], Muhamad Saufi bin Mohd Kassim[2], Samsuzana Binti Abd Aziz[2], Ramin Shamshiri[3], Farah Naz Akbar[4]and Muhammad Ibrahim[5]

[1]Department of Farm Machinery & Power, Faculty of Agricultural Engineering & Technology, University of Agriculture, Faisalabad (38040) Pakistan; [2]Department of Biological and Agricultural Engineering, Faculty of Engineering, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia; [3]Leibniz Institute for Agricultural Engineering & Bioeconomy, 14469, Germany. [4]Department of AHS, Sargodha Medical College, University of Sargodha (40100), Pakistan; [5]Department of Environmental Sciences & Engineering, Government College University Faisalabad (38000) Pakistan
***Corresponding author's e-mail: yamin529@uaf.edu.pk**

To practice the concept of site specific crop nutrient management on a large oil palm plantation, more soil samples are required to analyze the macronutrients. Most of the farmers in developing countries cannot afford the high cost of soil analysis. If fertilizers are applied by maintaining the desired NPK ratio in soil for a long time, then maintained ratio of NPK in the soil can help to estimate the deficiencies of NPK nutrients in the soil using oxidation-reduction potential. In this study, oxidation-reduction potential was recorded in chemical (NO_3^-, H_3PO_4, K^+) and aqueous fertilizer (NO_3^-, TSP, MOP) mixtures separately with the help of developed oxidation reduction potential (ORP) sensor and commercially available ORP meter (HM ORP-200). The calibration of developed ORP sensor in different concentrations of chemical (NO_3^-, H_3PO_4, K^+) mixture has a good correlation of 0.9923 with validation readings recorded in corresponding aqueous fertilizer (NO_3^-, TSP, MOP) mixtures with an error range of -0.44 to 1.72%. This small error range revealed that ORP sensor calibrated in chemical (NO_3^-, H_3PO_4, K^+) mixture of NPK nutrients can be used reliably in aqueous fertilizer (NO_3^-, TSP, MOP) mixture for the estimation of NPK nutrients. A good correlation of 0.9766 was also found between ORP sensor and commercially available ORP meter (HM ORP-200). Developed ORP sensor can be used for on-the-go operations in the soils of oil palm plantations because of its fast response time (<1 s) and notably high oxidation-reduction potential provided that required NPK ratios are maintained in the soil.
Keywords: Oil palm; NPK nutrients; ORP sensor; ORP meter; oxidation-reduction potential.
Abbreviations: FFB (Fresh Fruit Bunch), ISE (Ion Selective Electrodes), MOP (Murate of Potash), MSB (Most Significant Bit), NIRS (Near-Infrared Reflectance Spectroscopy), ORP (Oxidation Reduction Potential), TSP (Triple Super Phosphate).

INTRODUCTION

In the past, field variability led the researchers towards the concept of site specific crop nutrient management and it has been practiced at various levels by some farmers depending upon the available technology. Whelan, (2018) described the concept of site specific crop nutrient management as practical crop management having the impact on the soil nutrient variation and ultimately affecting the crop production. Various technologies are available for soil nutrient management, from soil sampling to fertilizer application to yield estimation. These tools improve the ability to fine-tune the nutrient management and establish a site-specific nutrition management plan for each area (Dass *et al.*, 2014). With the passage of time, concept of site specific crop nutrient management is being adopted by the large growers of oil palm gradually and farmers realized that mechanized fertilizer application can result in more efficient nutrient use and labor saving (PPI, 2018; MPOC, 2017: UCS, 2016; Rankine and Fairhust, 1999). However, a main issue in practicing site specific crop nutrient management is high cost of soil analysis which takes a long time after sending a soil sample to the commercial laboratories. To practice the concept on a big oil palm plantation extensive soil sampling is required to analyze the macronutrients and most of the farmers cannot afford it because of high cost.

Most of the oil palm plantations in Malaysia have undulated areas and with the rain water, nutrients may wash very easily and accumulate in lower areas (PPI 2018; MPCA, 2018; EPA, 2001). Therefore, oil palm growers require inexpensive, quick and reliable techniques to determine the soil nutrients and apply the desired nutrient in fertilizer deficient zone with the help of variable rate liquid fertilizer applicator. Ion selective electrodes (ISE) have good accuracy up to 95% to analyze the soil fast and accurate but equipment is costly and available commercially for N and K but not for P which need regular calibration with standard solutions (Adamchuk *et al.,* 2002; Adsett *et al.,* 1999). Other sensors like NIRS (Near-infrared reflectance spectroscopy) are expensive and require site-specific calibration, skills to operate and interpret the data (Sinfield *et al.,* 2010).

Since all forms of NPK nutrients (NH_4^+, NO_3^-, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}, K^+) are available to the plants as a result of parallel oxidation and reduction processes (MPCA, 2018). Therefore, oxidation reduction potential (ORP) or oxidation-reduction potential is a parameter to be determined for monitoring the oxidation and reduction process (DeLaune and Reddy, 2005; Vorenhout *et al.,* 2004). It can be used for on-the-go soil operations as inexpensive and indirect nutrients estimator. However, it may be only possible when nitrogen, phosphorus and potassium are present in the soil in desired ratio. Like other crop plants, oil palm consumes NPK in specific ratios at different stages of their growth. If NPK fertilizers are applied by maintaining in the ratios in the soil for the years, then maintained ratios can help to estimate the routine deficiencies of NPK nutrients in soil using oxidation-reduction potential. This is possible if very good soil management is practiced in plantation with regular soil testing for NPK. In this research, ORP sensor was developed, calibrated and validated in chemical (NO_3^-, H_3PO_4, K^+) and aqueous fertilizer (NO_3^-, TSP, MOP) mixtures for oil palm plantations. In addition, the characteristics of the developed ORP sensor were discussed in comparison with currently available ORP meters and sensors.

MATERIALS AND METHODS

Soil fertility standards for oil palm: Soil testing is an important part of a soil and plant nutrient management. It is a standard practice for farmers to determine the amount of fertilizer needed to meet the requirements of nitrogen, phosphorus, potassium and other nutrients in the crop (Faber *et al.,* 2007). Soil analysis helps to map the amount of macronutrients in the soil. According to the crop plant requirement, farmer can compute the needed amount of fertilizer to avoid the under or over dose.

International plant nutrition institute has fixed the general application rates for nitrogen, phosphorus (P_2O_5) and potassium (K_2O) based on fresh fruit bunch (FFB) analysis. These application rates have been mentioned in 'nutrient consumption' column of Table 1. It also shows the calculated standards for oil palm nutrition in the form of expected nutrients concentration in the soil and nutrient consumption ratios.

Development of oxidation-reduction potential (ORP) sensor: ORP sensor consists of two parts i.e. sensing element and its controller. Sensing element senses the NPK nutrients by monitoring the oxidation-reduction potential in the soil. The purpose of controller is to collect the reading of oxidation-reduction potential in mV and transmit to computer using USB cable.

***Theory of ORP sensing element*:** In this study, magnesium and iron electrodes were used to sense the oxidation-reduction potential of the soil, which ultimately leads to estimate the concentration of NPK nutrients in the soil. Magnesium and iron have standard reduction potentials of -2.37 V and -0.44 V respectively. The magnesium which has lower standard reduction potential acts as reducing agent and oxidation is carried out at that electrode. Thus, iron electrode becomes anode. On the other hand, iron having higher standard reduction potential becomes oxidizing agent and net reduction occurs at magnesium electrode named as cathode (Delaune and Reddy, 2005). The above statements can be explained by the following equations (1, 2, and 3) which show the oxidation and reduction processes with reduction potentials.

$$Mg \rightarrow Mg^{2+} + 2e^- \quad \text{(Oxidation reaction, } E°_{anode} = -2.37 \text{ V)} \quad (1)$$

$$Fe^{2+} + 2e^- \rightarrow Fe \quad \text{(Reduction reaction, } E°_{cathode} = -0.44 \text{ V)} \quad (2)$$

$$Mg + Fe^{2+} \rightarrow Mg^{2+} + Fe \quad \text{(Net reaction)} \quad (3)$$

Equation (4) shows net potential or maximum measureable potential difference of 1.93 V (1930 mV) between cathode and anode.

$$E°\ net = E°_{cathode} - E°_{anode} = -0.44-(-2.37) = 1.93V \text{ or } 1930mV \quad (4)$$

Where; $E°_{net}$ is net potential or maximum potential difference between cathode and anode, (V), $E°_{cathode}$ is standard reduction potential of cathode, (V), $E°_{anode}$ is standard reduction potential of anode, (V)

Thus, oxidation-reduction potential was monitored to estimate the NPK nutrients in the soil by the magnesium and iron electrodes of 10 mm long and 3 mm diameter. These electrodes act as a sensing element of ORP sensor (Figure 1).

Table 1. Macronutrients required by oil palm based on FFB analysis.

Nutrient	Nutrient consumption (kg/palm/year)	Nutrient consumption (ppm/year)	Consumption ratio w.r.t P_2O_5	Expected in soil (ppm)
Available N	0.493*	88	2.94	59
NO_3^-	2.184	390	13.00	260
P_2O_5	0.168*	30	1.00	20
K_2O	0.747*	133	4.44	89

*(Rankine and Fairhust, 1999)

Figure 1. ORP sensor and its electrodes

Design of controller for ORP sensor**:** Interfacing of ORP electrodes with a controller was necessary to monitor and record the readings in mV. Design of controller was based on AT89S52 microcontroller and ORP electrodes were interfaced with the controller using ADC0831 which is a single channel serial analog to digital converter configurable with the help of programming (Fig. 2). Voltage reference input in ADC0831 was adjusted at 1000 mV to allow encoding at smaller analog voltage span to the full 8 bits' resolution of (3.906 mV). Figure 3 shows the programming algorithm to record the oxidation-reduction (redox) potential using controller which further can convert the redox values to NPK concentrations based on calibration of ORP sensor. V_{IN} (+) line of ADC0831 was attached with the positive terminal of ORP sensor (Mg electrode) because oxidation occurs at Mg electrode in the soil (Figure 2). Similarly, V_{IN} (-) line was attached with Fe electrode which acts as an acceptor of electrons within the soil i.e. negative terminal or ground. Register 'R3' of microcontroller was used to create the loop of operation performed to receive 8 data bits from ADC0831. Every digital value from ORP sensor was saved in allocated memory location (R4) and transmitted to computer with the help of accumulator of microcontroller.

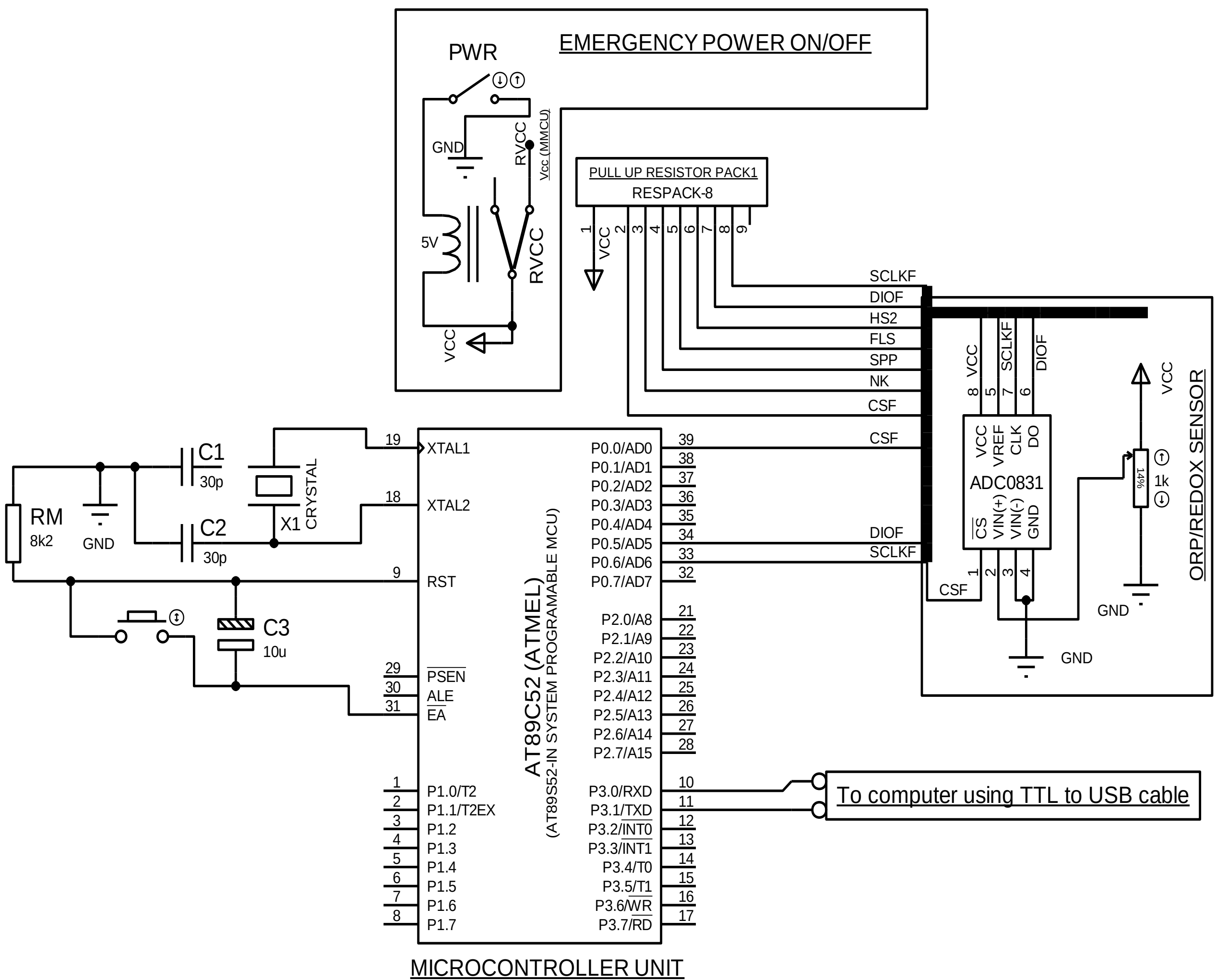

Figure 2. Design of controller for ORP sensor

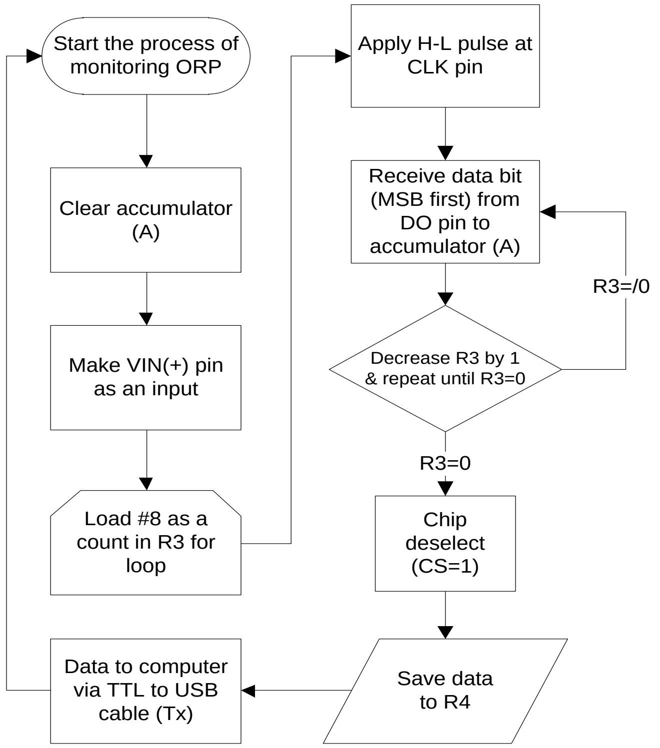

Figure 3. Programing algorithm of getting fertility data from ORP sensor

Calibration and validation procedure of ORP sensor: Oxidation-reduction potential can be calibrated with NPK concentrations in standard ratios which are required by the oil palm. The calibration was performed with the concentrations of NPK considered in terms of NO_3^-, P_2O_5 and K_2O as shown in Table 1. Nitrate and potassium concentrations were prepared with standard calibration solution of NO_3^- (2000 ppm) and K^+ (2000 ppm) from Horiba (Figure 4). Similarly, phosphorus concentrations in terms of P_2O_5 were prepared with 85 % H_3PO_4 solution (Figure 4). All solutions were mixed in specific NPK ratios mentioned in nutrient concentration columns of Table 2 and oxidation-reduction potential in chemical mixture was recorded using ORP sensor. Then calibration of ORP sensor performed in chemical mixture of NPK nutrients was verified by monitoring the oxidation-reduction potential in fertilizer mixture of same concentrations prepared by mixing the NO_3^-, P_2O_5 as triple super phosphate [$Ca(H_2PO_4)_2$] and K_2O as murate of potash (KCl) at recommended ratios for oil palm (Table 2). It is to note that triple super phosphate (TSP) contains 46% P_2O_5 and murate of potash (MOP) contains 60% of K_2O. Since urea fertilizer (46% N) doesn't contain NO_3^- and takes time for conversion to NO_3^- through nitrification process in the soil medium, therefore, Horiba NO_3^- solution was used for ORP validation purposes. Further, the recorded oxidation-reduction potential in aqueous fertilizer mixture was correlated with the oxidation-reduction potential noted during the calibration of ORP sensor in known chemical mixture of NPK nutrients.

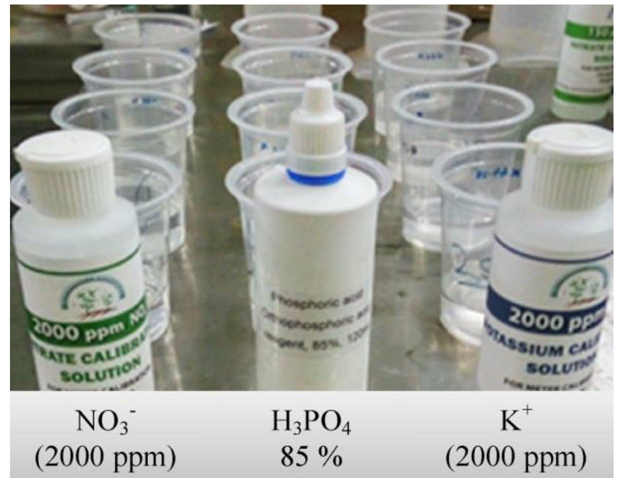

Figure 4. Solutions used for calibration and validation of ORP sensor

Table 2. Nutrient concentrations in chemical and aqueous fertilizer mixtures

Sample		Nutrient concentration			
		NO_3^-	N	P_2O_5	K_2O
		ppm	ppm	ppm	ppm
	↓NCF*|Ratio→	13	2.94	1	4.44
1	4	52	12	4.0	18
2	8	104	24	8.0	36
3	12	156	35	12.0	53
4	16	208	47	16.0	71
5	20	260	59	20.0	89
6	24	312	70	24.0	107
7	28	364	82	28.0	124
8	32	416	94	32.0	142
9	36	468	106	36.0	160
10	40	520	117	40.0	178
11	44	572	129	44.0	196

*NCF is nutrient concentration factor

RESULTS AND DISCUSSION

Calibration and validation of ORP sensor: Oxidation-reduction potential data obtained during the calibration and validation process was plotted separately against available nitrogen, P_2O_5 and K_2O (Figure 5, 6 and 7). Model equations with $R^2 = 0.9896$ were also developed for conversion between oxidation-reduction potential and respective nutrient concentration in the soil provided that NPK ratios (Table 1) are maintained in the soil of oil palm plantation. These equations are not valid for abnormal NPK ratios in the soil of oil palm plantation. For abnormal NPK ratios, calorimetric technique or laboratory results may be used in variable rate liquid fertilizer applicator. It was revealed from Table 3 that an error of -0.44 to 1.72% (-8 to 33 mV maximum) existed in the mean values of oxidation-reduction potential measured in aqueous fertilizer mixtures with respect to that of the chemical mixtures. This small error range reveals that ORP sensor calibrated in chemical (NO_3^-, H_3PO_4, K^+) mixture of NPK nutrients can be used reliably in aqueous fertilizer (NO_3^-, TSP, MOP) mixture for estimation of NPK nutrients like YSI ORP sensors which have accuracy of ±20 mV. It was also found that calibration readings of ORP sensor in different concentrations of chemical (NO_3^-, H_3PO_4, K^+) mixture has a good correlation of 0.9923 with the validation readings recorded in the corresponding aqueous fertilizer (NO_3^-, TSP, MOP) mixtures (Table 3).

A reasonable correlation of 0.9766 was also found in the readings of commercially available ORP meter (HM ORP-200) and ORP sensor developed in this research for chemical ((NO_3^-, H_3PO_4, K^+) mixture (Table 3 and Figure 8). It is clearly noted in Figure 8 that developed ORP sensor gives notable higher oxidation-reduction potential for different nutrient concentrations in the chemical ((NO_3^-, H_3PO_4, K^+) mixture as compared to the laboratory ORP meter (HM ORP-200). Developed ORP sensor can also be used for on-the-go soil operations because of its fast response (<1 s) compared to the laboratory ORP meter (HM ORP-200). ORP meter (HM ORP-200) has varied response time depending upon the ionic activity with a measurement range of -999 to 1000 mV like WQ600 ORP sensors which need warm up time of 3 seconds minimum with the measurement range of ±500 mV. Lin *et al.*, (2017) built a platinum based multifunctional sensor which was able to measure ORP in a short range of 150 to 800 mV in aqueous solution with R^2 = 0.9875 compared to the 1930 mV measurement range at 3.906 mV resolution of developed ORP meter with R^2 = 0.9896. Similar type of OPR sensor was also developed by Shitashima *et al.* (2005) having a platinum electrode for sea water tests responding with in 1 s with long-term stability which is comparable with newly developed ORP sensor having response time of <1 s.

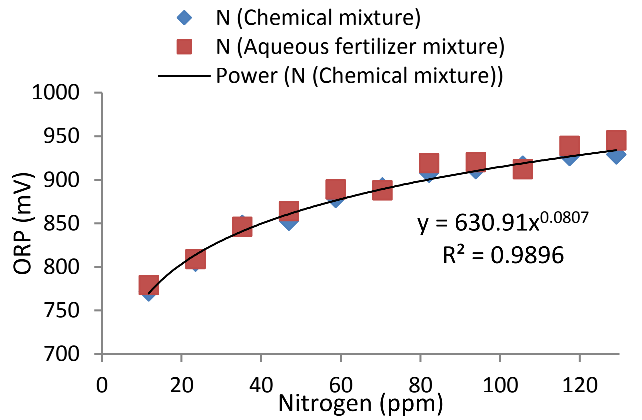

Figure 5. Relation of ORP and available nitrogen in chemical (NO_3^-, H_3PO_4, K^+) and aqueous fertilizer (NO_3^-, TSP, MOP) mixtures

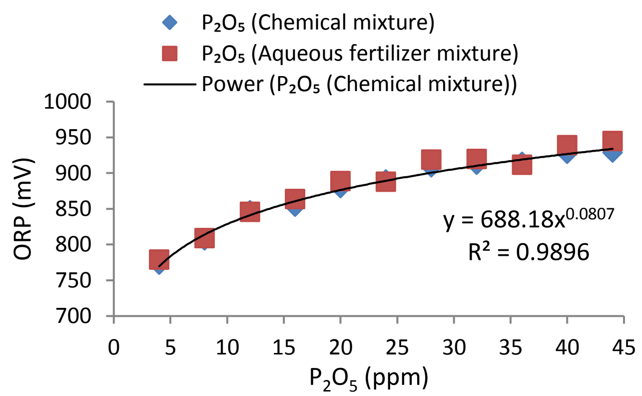

Figure 6. Relation of ORP and P_2O_5 in chemical (NO_3^-, H_3PO_4, K^+) and aqueous fertilizer (NO_3^-, TSP, MOP) mixtures

Table 3 . Calibration and validation of ORP sensor

Sample		Nutrient concentration				HM ORP-200 reading in chemical mixture	ORP sensor reading in chemical mixture	ORP sensor reading in aqueous fertilizer mixture	Error of readings in aqueous fertilizer mixture w.r.t chemical mixture
		NO_3^-	N	P_2O_5	K_2O				
		ppm	ppm	ppm	ppm	mV	mV	mV	%
	↓NCF*|Ratio→	13	2.94	1	4.44	Mean	Mean	Mean	-
1	4	52	12	4.0	18	460	772	779	0.91
2	8	104	24	8.0	36	466	806	809	0.37
3	12	156	35	12.0	53	468	848	846	-0.24
4	16	208	47	16.0	71	470	853	864	1.29
5	20	260	59	20.0	89	470	879	889	1.14
6	24	312	70	24.0	107	471	891	888	-0.34
7	28	364	82	28.0	124	473	908	919	1.21
8	32	416	94	32.0	142	473	912	920	0.88
9	36	468	106	36.0	160	474	916	912	-0.44
10	40	520	117	40.0	178	476	927	939	1.29
11	44	572	129	44.0	196	476	929	945	1.72

*NCF is nutrient concentration factor

r= 0.9923

r= 0.9766

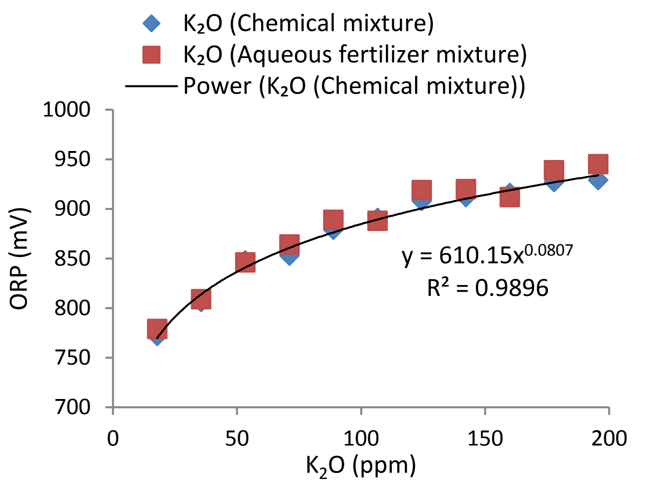

Figure 7. Relation of ORP and K_2O in chemical (NO_3^-, H_3PO_4, K^+) and aqueous fertilizer (NO_3^-, TSP, MOP) mixtures

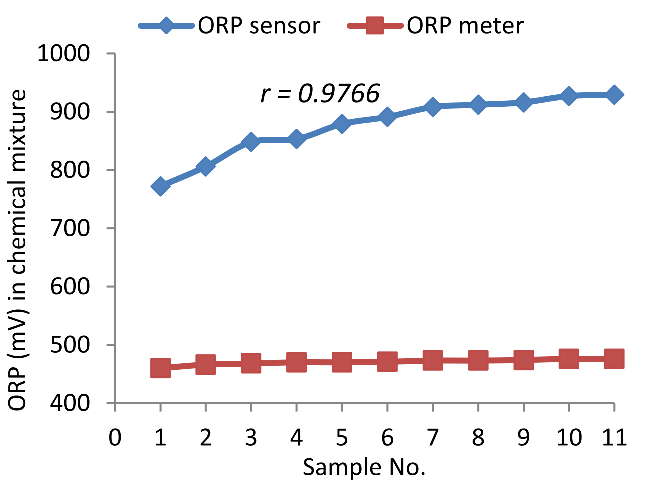

Figure 8. Correlation of ORP sensor values with ORP-200 meter values in chemical (NO_3^-, H_3PO_4, K^+) mixture

***Conclusion and recommendations*:** Calibration of ORP sensor in different concentrations of chemical (NO_3^-, H_3PO_4, K^+) mixture has a good correlation of 0.9923 with validation readings recorded in corresponding aqueous fertilizer (NO_3^-, TSP, MOP) mixture with an error range of -0.44 to 1.72%. The correlation and small error range indicates ORP sensor calibrated in chemical (NO_3^-, H_3PO_4, K^+) mixture can be used reliably in aqueous fertilizer (NO_3^-, TSP, MOP) mixture for the estimation of NPK nutrients. When fertilizers are applied by maintaining the desired NPK ratios in soil for the years then maintained ratios can help to estimate the deficiencies of NPK nutrients in soil using oxidation-reduction potential. Developed model equations for conversion between oxidation-reduction potential and respective nutrient concentration in the soil are useful, provided that the required NPK ratios are maintained in the soil of oil palm plantation. These equations are not valid for abnormal NPK ratios in the soil of oil palm plantation. For abnormal NPK ratios in the soil, colorimetric technique or laboratory results may be used. Further, considerably higher oxidation-reduction potential for different nutrient concentrations in the chemical (NO_3^-, H_3PO_4, K^+) mixture was noted with the developed ORP sensor compared to the laboratory ORP meter (HM ORP-200). Due to fast (<1 s) and better notable response compared to the ORP meter (HM ORP-200) and WQ600 ORP sensors, the developed ORP sensor can be considered for on-the-go soil measurements.

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