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***NEKAZARITZAKO INGENIARITZAKO ETA BIOZIENTZIETAKO GOI
MAILAKO ESKOLA TEKNIKOA***

EVALUATION OF NITRATE SOIL PROBES

presentado por

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INGENIARITZAN***

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Abstract

The production and utilization of the chemical N fertilizers have played a great role in increasing crop yield and meeting the demand of population growth. Nitrate (NO_3^-) is the common form of nitrogen absorbed by plants, and the most abundant source of N in soils. It has high solubility in water and low retention by soil particles so it is prone to leaching and seriously polluting biological environments and people health. European regulations are becoming more aware due to its secondary effects, so it is therefore of great interest to optimize the nitrogen fertilizer applied. There are few methods to know the amount of nitrate in the soil. The development of ion selective sensors provides knowledge of the dynamics of nitrate in the soil in real time which can be very useful for nitrate management.

The objective of this study is to analyze the performance of three probes under the same conditions. The commercial probes used were JXCT, RIKA and Nutrisens. Three probes of each model were used. The performance was analyzed with respect to electrical conductivity (0-50 mS/cm), nitrate concentration in aqueous solution and in sandy soil (0-180 ppm NO_3^-) at different volumetric moisture contents (0-35%).

To analyze the effect of electrical conductivity on the readings, sodium chloride solutions were used. The results showed that Nutrisens probes are slightly affected by electrical conductivity because the chloride ion is confused with the nitrate ion due to the similarities between the two ions. The RIKA and JXCT probes showed high variability and inconsistency with respect to the readings, making these probes highly sensitive. In the evaluation of nitrate concentration in liquid solution, all probes proved to be highly sensitive with a coefficient of determination above 0.95. In the evaluation of nitrate concentration at different moisture content in sandy soil, it is concluded that the Nutrisens probe is the one that best responds to the tests, while RIKA and JXCT show very little sensitivity in their readings.

The Nutrisens probe is designed to measure the nitrate trend and therefore performs well in all tests, while the RIKA and JXCT probes are designed to measure the exact nitrate concentration and therefore only perform well in liquid solution.

This study has allowed to start analyzing the behavior of the probes, but it would be of great interest to analyze them in different types of soils since we have started with a sandy soil which is the most homogeneous and less complex soil.

Keywords: nitrate, soil sensors, electrical conductivity, nitrate solution, moisture content

Resumen

La producción y utilización de los fertilizantes químicos de N han desempeñado un gran papel en el aumento del rendimiento de los cultivos y en la satisfacción de la demanda del crecimiento de la población. El nitrato (NO_3^-) es la forma común de nitrógeno absorbida por las plantas y la fuente más abundante de N en los suelos. Tiene una alta solubilidad en el agua y una baja retención por parte de las partículas del suelo, por lo que es propenso a la lixiviación y a contaminar gravemente los entornos biológicos y a perjudicar la salud de las personas. La normativa europea es cada vez más restrictiva por sus efectos secundarios, por lo que es de gran interés optimizar el abono nitrogenado aplicado. Existen pocos métodos para conocer la cantidad de nitrato en el suelo. El desarrollo de sensores iónicos selectivos permite conocer la dinámica del nitrato en el suelo en tiempo real, lo que puede ser muy útil para la gestión del nitrato.

El objetivo de este estudio es analizar el rendimiento de tres sondas en las mismas condiciones. Las sondas comerciales utilizadas fueron JXCT, RIKA y Nutrisens. Se utilizaron tres sondas de cada modelo. Se analizó el rendimiento con respecto a la conductividad eléctrica (0-50 mS/cm), la concentración de nitrato en solución acuosa y en suelo arenoso (0-180 ppm NO_3^-) con diferentes contenidos de humedad volumétrica (0-35%).

Para analizar el efecto de la conductividad eléctrica en las lecturas, se utilizaron soluciones de cloruro sódico. Los resultados mostraron que las sondas Nutrisens se ven ligeramente afectadas por la conductividad eléctrica porque el ion cloruro se confunde con el ion nitrato debido a las similitudes entre ambos iones. Las sondas RIKA y JXCT mostraron una alta variabilidad e inconsistencia con respecto a las lecturas, lo que hace que estas sondas sean muy sensibles. En la evaluación de la concentración de nitrato en solución líquida, todas las sondas demostraron ser altamente sensibles con un coeficiente de determinación superior a 0,95. En la evaluación de la concentración de nitratos a diferentes contenidos de humedad en suelos arenosos, se concluye que la sonda Nutrisens es la que mejor responde a las pruebas, mientras que RIKA y JXCT muestran muy poca sensibilidad en sus lecturas.

La sonda Nutrisens está diseñada para medir la tendencia del nitrato y, por tanto, responde bien en todas las pruebas, mientras que las sondas RIKA y JXCT están diseñadas para medir la concentración exacta de nitrato y, por tanto, sólo responden bien en solución líquida.

Este estudio ha permitido empezar a analizar el comportamiento de las sondas, pero sería de gran interés analizarlas en diferentes tipos de suelos ya que hemos empezado con un suelo arenoso que es el más homogéneo y menos complejo.

Palabras clave: nitrato, sensores de suelo, conductividad eléctrica, solución de nitrato, contenido de humedad

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1. INTRODUCTION

Agricultural systems are nitrogen (N) deficient throughout the world. Various plant molecules such as amino acids, chlorophyll, nucleic acids, ATP, and phyto-hormones, that contains nitrogen as a structural part, are necessary to complete the biological processes, involving carbon and nitrogen metabolisms, photosynthesis, and protein production (Frink et al., 1999). It is involved in various critical processes, such as growth, leaf area-expansion and biomass-yield production. The production and utilization of the chemical N fertilizers have played a great role in increasing crop yield and meeting the demand of population growth.

Nitrogen exists in the soil system in many forms and transforms very easily from one to another. Most of the nitrogen available in the soil is unavailable for the plants and needs to be transformed into nitrate or ammonium (NH_4^+) which are the available forms for plant up take. The route N follows in and out of the soil system is collectively called nitrogen cycle (Figure 1). The N cycle is biologically influenced, and the biological processes are influenced by prevailing climatic conditions along with a particular soil's physical and chemical properties. The main processes of the N cycle are fixation, mineralization, immobilization, nitrification, and denitrification. Depending on the dynamics of the cycle and the inputs added (fertilizers), the amount of nitrate in the soil will be different. Nitrate (NO_3^-) is the most abundant source of N that is available for plants in cultivated soils, and it is the common form of nitrogen absorbed by plants growing in the field (Andrews et al., 2013).

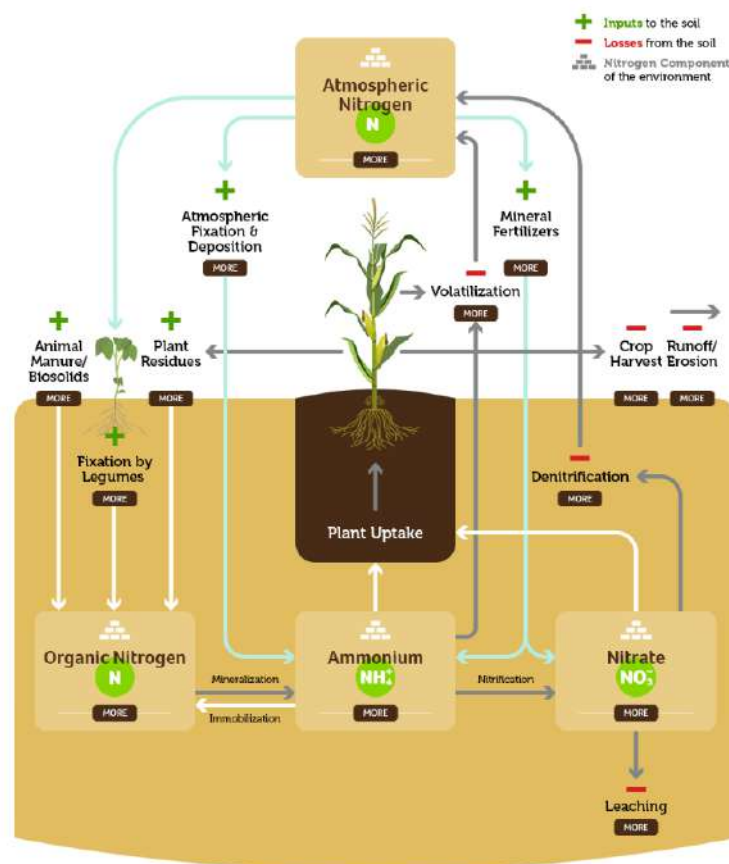


Figure 1. The Nitrogen Cycle (Source: Nutrien, 2022).

Nitrate pollution of water resources may originate from several different pathways, including point (such as wastewater effluents and intensive livestock farming) and diffuse (such as fertilizers, extensive livestock farming, atmospheric deposition, etc.) sources. However, up to now, nitrate pollution from agricultural diffuse sources has been considered the main cause of groundwater degradation in the European Union (EU) (Groeneveld et al., 1998; De Roo, 1980; Sutton et al., 2011) due to its high solubility in water and low retention in soil by soil particles, it is prone to leaching to the subsoil layer and ultimately to the ground water, if not taken up by plants or denitrified to N_2O and N_2 . It can seriously threat people health and pollute biological environments accelerating eutrophication, causing dramatic increases in aquatic plant growth and changes in the types of plants and animals that live in the stream.

Within the EU, the reduction and prevention of water pollution caused by nitrate from agricultural sources was addressed by the Nitrate Directive 91/676/EEC. This directive establishes that both surface freshwaters and groundwater should be considered affected by nitrate pollution when they contain more than 50 mg L^{-1} of nitrate. The recommended limit for nitrate in drinking water and for the eutrophication of freshwaters is 25 mg L^{-1} .

In addition, inappropriate use of nitrogen fertilizers can also have an economic impact. The optimum dose of nitrogen that must be provided to a crop depends on three factors: the crop, the fertility of the soil and the goal that wants to be achieved. Therefore, in most of the cases, the decision to use a certain dose cannot be made from the calculation of the extractions carried out by the crop, as has been done for many years, following the classic recommendations on fertilization in agriculture (Durán et al., 2010). When N inputs to the soil system exceed crop needs, there is a possibility that excessive amounts of nitrate may enter either ground or surface water. The optimum dose to apply can depend on the environmental benefit, economic benefit, or production. The dose of N based on the environmental benefit is always going to be less than the economical and production dose (Figure 2).

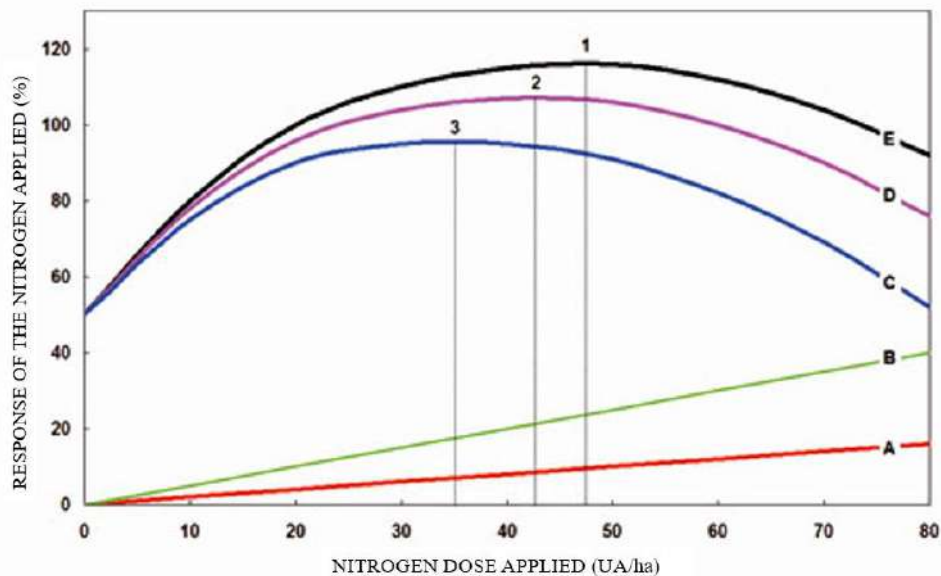


Figure 2. Analysis of the optimum doses of nitrogen application: Agronomic (1), economic (2) and environmental (3). Curves: A, cost of N applied; B, environmental cost of N applied; C, environmental benefit; D, agricultural economic benefit; E, gross production (Source: Durán et al., 2010).

In order to make a good recommendation of the amount of nitrogen fertilizer to add, it is advisable to study the crop and climatological characteristics of the area as well as those of the soil at the time prior to fertilization and apply the following formula.

$$\text{Fertilizer } N_{\text{needed}} = \frac{\text{Total N need based on potential yield}}{\text{on potential yield}} - \left(\frac{\text{Mineralizable N}}{\text{Mineralizable N}} + \frac{\text{Soil test N}}{\text{Soil test N}} \right) \quad (1)$$

Total N need based on potential yield is based on the field's long-term average yield and on the annual precipitation. Mineralizable nitrogen vary in the soil capacity to release N from organic matter during the growing season. The amount released depends on the factors such as the amount of soil organic matter, tillage practice, and soil temperature during the growing season (Mahler, 2015).

Nitrate analysis is something that has been done for a long time in liquid mediums. For its detection in water there are several methods both in-situ and laboratory based. The detection methodologies can be electrochemical detection, chromatography detection, electromagnetic detection, biosensors, UV (ultraviolet) sensors or fibre-optic sensors (Alahi & Mukhopadhyay, 2018). As can be seen, there is a wide range of options analyzing nitrate concentrations in water.

Few methods are available to analyze the mineralizable N in the soil. The classical method consists of determining mineralizable N by soil sampling and subsequent laboratory analysis. The main problem with the soil test is its high economic cost, the need to carry out a good soil sampling as well as the time it takes for the samples to be analyzed. Rapid methods have also been developed to estimate it. The first one consists of a soil sampling and a quick analysis. This method is fast and does not require a laboratory, although it requires a previous analysis to establish certain parameters of the soil to be analyzed. The second type consists of the installation of probes such as lysimeters, they extract the solution from the soil matrix for subsequent rapid analysis or by colorimetry or spectrometry. Finally, and most innovative are the sensors. Few sensors are beginning to emerge to measure in-situ and in real time.

To our knowledge, to date there is no study comparing different soil sensors under the same testbed. These probes can help to know more accurately and in real time the trend of nitrate in the soil as well as its concentration at a moderate cost. The control of nutrients with sensors will permit an optimization of irrigation and fertilization management systems and thus will be useful for reducing the environmental impact caused by the runoff of nutrients into surface and groundwaters.

2. AIMS

To date, to the best of our knowledge, the few nitrate sensors available have not been evaluated under the same experimental setup.

The main objective is to analyze the behavior of the following nitrate sensors: Nutrisens sensor (Verde Smart Co.); NPK sensor RK520-05 (Hunan Rika Electronic Tech Co.); and NPK sensor (JXCT) (Figure 3).

Sub-objectives:

1. Evaluate the selectivity of the sensors, analyzing the selectivity of nitrate ion signal with the electrical conductivity.
2. Evaluate the sensitivity of the sensors to nitrate ion in aqueous solution.
3. Evaluate the response of the probes in a soil (sandy soil) to changes in moisture and nitrate concentration of the solution.

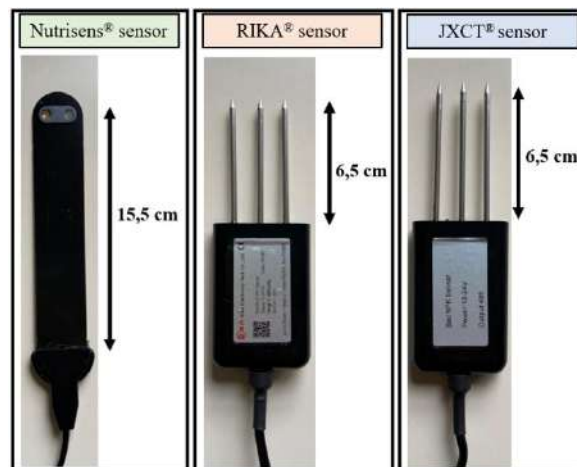


Figure 3. Sensors used in the experiment.

3. MATERIALS AND METHODS

3.1 Sensors

The evaluated sensors are based on different principles.

The Nutrisens sensor measures nitrate and potassium ions, and is based on electrochemical detection. Electrochemical sensors are based on several electrochemical reactions at the surface of an electrode. According to the various modes of signal transduction, electrochemical sensors are normally classified as potentiometric, amperometric/voltametric, and impedimetric/conductimetric systems (Gellings, 2019; Mahmud et al., 2020; Power & Morrin 2013).

This sensor is based on an Ion Selective Electrode (ISE). According to the recommended definition of the International Union of Pure and Applied Chemistry (IUPAC), ISE is an electrochemical sensor whose potential response has a linear relationship with the logarithm of specific ionic activity in the solution. The potential of one single ion selective electrode cannot be directly measured and a reference electrode whose potential remains constant is needed to put into test solution together to form a two-electrode system Figure. Ion selective membrane is the key component of ion selective electrode. Due to the differences of ionic activity (concentration), ion exchange happens on the surface of both sides of ion selective membrane to form membrane potential (Zhang et al., 2013).

For the adjustment with these sensors there is a linear and a nonlinear adjustment. Both adjustments are logarithmic, but the non-linear adjustment uses all the points (Nikolskii-Eisenman equation) and the linear adjustment (Nernst equation) only the linear part of the logarithmic fitting, this last adjustment is the one used in the evaluation of the probes.

In the case of the Nutrisens sensor measures the nutrient concentration trend and not the nutrient concentration. Due to the heterogeneity of the soil, it can not be calibrated in reliably, but it can be calibrated in solution.

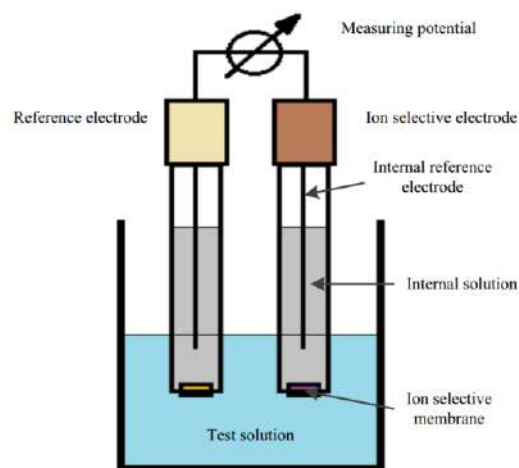


Figure 4. Two electrode detection system (Source: Zhang et al., 2013).

The Nutrisens sensor is made up of the probe and a signal adaptation electronics (Figure 5).

In the probe, in its lower part of the black face is the sensor area, where there is a gelatinous material that is the most sensitive part and although it is protected, care must be taken not to hit this area in the time of installation. The probe must be connected to the signal adaptation electronics through the corresponding connector. It can be connected in analogic or digital mode. For the digital mode, the one used, the SDI12 module, also known as SDIAN, must be connected between the signal adaptation electronics of each of the probes and the datalogger Campbell CR10X.

Its development and patent (Alonso & Arasa, 2020) took several years to develop the Spanish company Verde Smart with the Autonomous University of Barcelona (UAB).

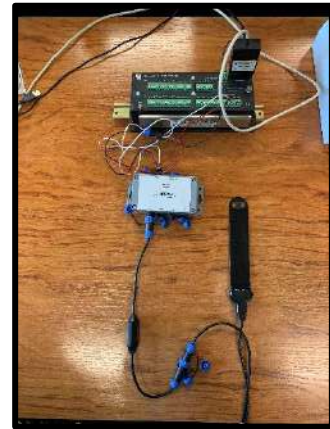


Figure 5. Nutrisens sensor connection with signal adaptation electronics, SDIAN and Campbell CR10X.

The RIKA and JXCT soil sensors correspond to two Chinese companies and are suitable for detecting the content of nitrogen, phosphorus and potassium. The physical principle of measurement is unknown as there is no documentation. Information was requested from the manufacturers but has not been provided. Based on Longhurst & Nicholson (2020), we assume that these probes are conductimeters and measure the electrical conductivity and with an equation they relate and derive the concentration of the ions. Both sensors have similar measurement parameters, the communication protocol is RS485 carried out with Arduino, and they are powered with a 12V DC power supply. These probes are already calibrated by default by the company (Appendix 1) and the measurements are in mg/kg. The calibration equation is unknown and embedded by the manufacturer in the probe, so the raw electrical measurement signal is not available.

3.2 Evaluation of electrical conductivity (EC)

This test consists of evaluating the effect on the probe output signal by analyzing the nitrate ion signal in relation to the EC in the absence of nitrate.

To probe that, one liter of deionized water (from which the cations and anions have been extracted to prevent them from influencing the sensor readings) was used and increments of 5 grams of sodium chloride (NaCl) up to 35 grams corresponding to the salinity of seawater were added. The electric conductivity of each solution was measured (Table 1) with a conductivity meter.

Then, measurements were taken (Figure 6). One probe of Nutrisens and three probes of RIKA and JXCT were used. One reading was made at each EC solution. The probes need to stabilize in the medium, so for the JXCT and RIKA the measurements were taken after one minute and the Nutrisens after 5 minutes. Between solutions the probes were washed with deionized water.

Table 1. Amount of NaCl added for each electric conductivity (EC).

EC (mS/cm)	2.22	3.81	5.40	6.99	8.58	10.17	13.35	16.53	24.47	32.42	40.36	48.31	56.26
Amount of NaCl (g)	1	2	3	4	5	6	8	10	15	20	25	30	35

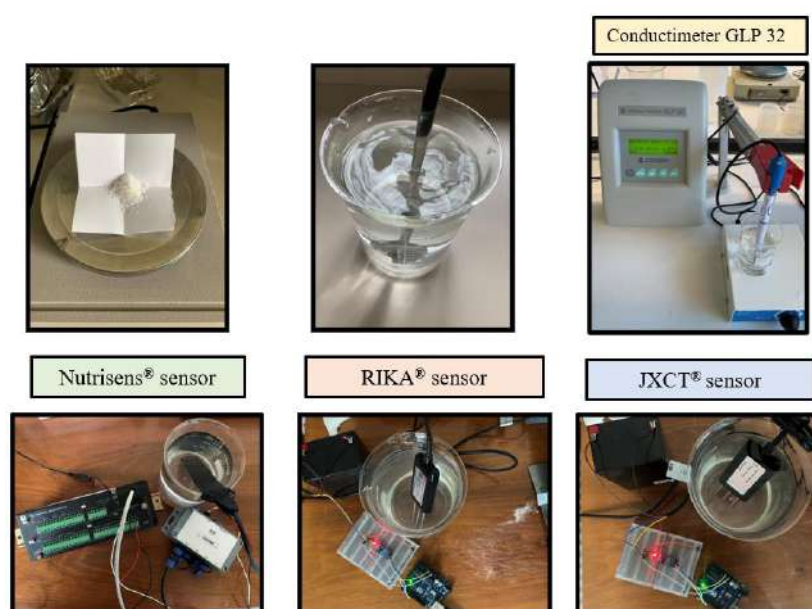


Figure 6. Experimental set-up of EC.

3.3 Evaluation of nitrate concentration in liquid medium

The objective of this test is the evaluation of the sensors under controlled laboratory conditions in a liquid medium using deionized water solutions and standard nitrate solutions. As starting material, three solutions of nitrogen nitrate were used (44 mg NO_3^- /l, 100 mg NO_3^- N/l y 1000 mg NO_3^- /l) (HACH® and Supelco®), which were diluted into 12 different concentrations between 0 and 180 mg NO_3^- (range of agronomic interest).

Then, measurements were taken (Figure 7). One probe of each type was used, and five readings were made at every nitrate concentration solution. Between solutions the probes were washed with deionized water. The probes need to stabilize in the medium, so for the JXCT and RIKA the measurements were taken after one minute and the Nutrisens after 5 minutes.

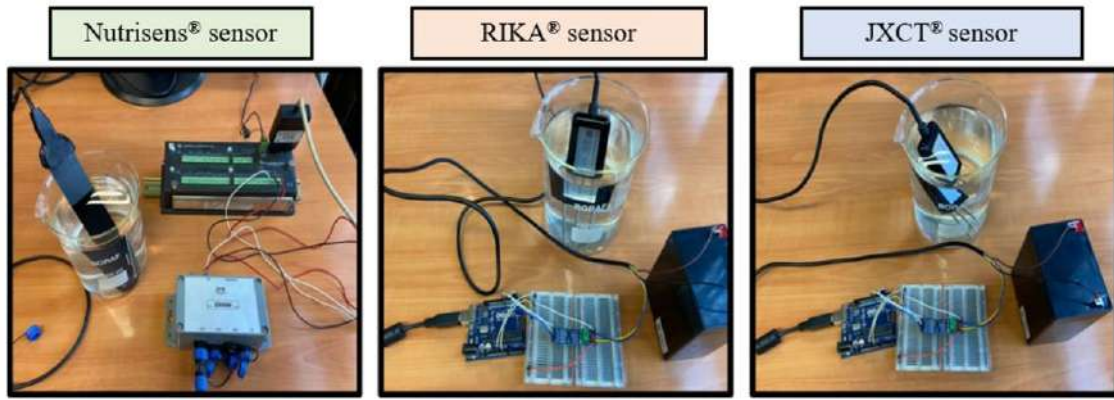


Figure 7. Experimental set-up in dissolutions.

3.4 Evaluation of nitrate concentration in sandy soil

The objective of this test is to evaluate for the first time, in a controlled and homogeneous soil (sandy soil), the effect of the nitrate ion concentration on the dissolution of the soil matrix and the moisture content on the electrical signals of the probes analyzed.

The type of soil used during the test was a siliceous sandy soil with a 0,2-0,7 mm grain size. This type of soil was chosen due to its homogeneity, no structure and ease of handling which made the added solution to be distributed homogeneously.

The first step was to prepare the different soil samples. It begun by drying the sand in the oven at 110°C for 24 hours to obtain a moisture content of 0%. Once the sand was dried, the volumetric humidity was determined as the measurement reference. This is calculated from the ratio between the volume of the liquid fraction and the volume of the sample, applying the following formula:

$$\theta = \frac{V_w}{V_s} \quad (2)$$

Where:

θ : Volumetric humidity (%)

V_w : water volume (ml)

V_s : soil sample volume (ml)

In the case study, to calculate the humidity, one liter of water was introduced into a container and that water level was marked with a sharpie. Then, the water was removed, and the container was dried to place it over a scale and the sand was poured up to the mark. The weight of the sand was recorded to add the same amount of it to the other containers, in this case 1400,5 grams (Figure 8).



Figure 8. Steps for determining the volume.

According to Oates et al. (2017) the measured capacitance is altered by the soil temperature and the temperature of the critical components in the measurement circuits. This factor must be considered since the sand was at 110°C in the oven, so it must be cooled for 24 hours so that it reaches room temperature.

The second step was to make the dissolutions. Three nitrogen nitrate solutions were used as a starting material (44 mg NO_3^-/l , 100 mg $\text{NO}_3\text{N}/\text{l}$ y 1000 mg NO_3^-/l) (HACH® and Supelco®) which were diluted at different concentrations between 0 and 150 mg $\text{NO}_3^- \cdot \text{L}^{-1}$ (agronomic interest range). The water used to make the solutions was deionized water.

The studied concentrations were 10, 25, 50, 75 and 150 ppm. One liter of each solution at those concentrations was made to increase the humidity of the sand. To check that the solutions were made correctly a nitrate meter from HORIBA® was used (Figure 9). The meter had to be calibrated in advance with two standard solutions, 150 ppm and 2000 ppm. Once it was calibrated the meter was very accurate.



Figure 9. LAQUAtwin NO_3^- IIC meter from HORIBA® (Source: Horiba, 2022).

Once the containers with the dried soil and the solutions were prepared, it was proceeded to obtain the desired volumetric humidity in the different soil samples. The test consisted of five samples with a certain nitrate concentration where the humidity increased by 5% from 5% to 35%. Data was first taken at 0% moisture (dried sand), then 50 ml of the different solutions were added to create 5% moisture (Figure 10) and then the data was collected with the different soil sensors. The increments of 50 ml were added to increase the humidity by 5% each time, until reaching 35% (sand saturation) (Table 2) and the sand was compacted every trial in order to maintain the volumetric humidity.

Three probes of each type were used and three lectures per probe and trial were done. Nurisens probe readings were obtained by first inserting the probe and then compacting the soil around and then waiting 5 minutes until the probes stabilized. For the JXCT and Rika probes readings, the sand was first compacted and then the probe was inserted to the point where the sensor part was completely covered. The readings of the probes were taken after 15 seconds.



Figure 10. Experiment set up for 5% moisture.

Table 2. Amount of dissolution added for each moisture content.

Humidity content in the sample	0%	5%	10%	15%	20%	25%	30%	35%
Volume of solution applied with different [NO ₃ -]	0 ml	50 ml	+50 ml (100 ml)	+50 ml (150 ml)	+50 ml (200 ml)	+50 ml (200 ml)	+50 ml (200 ml)	+50 ml (200 ml)

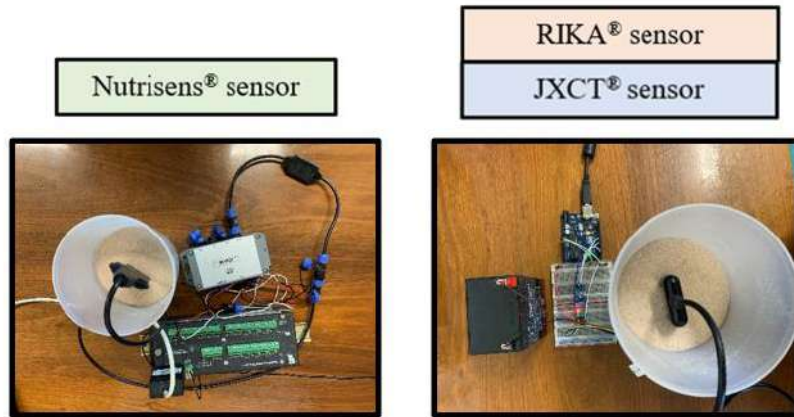


Figure 11. Process of reading of the probes in sandy soil.

3.5 Calibration

If it is desired to know the exact concentration of nitrate, these sensors need a soil-specific calibration due to each soil type having a different amount of clay and cation exchange capacity. Therefore, it is not reliable to use standard formulas to give the nitrate concentration, so it is advisable to calibrate the probe for each soil type, although in an unreliable way due to the heterogeneity of the soil. The calibration method will be linear or non-linear depending on the response dynamics of the probes and the adjustment method will be by least squares.

The Nurisens sensor provides the readings in millivolts and needs a calibration equation for each single probe according to the manufacture company since the sensor membrane varies from one probe to the other. Although this probe is designed to see what the nitrate trend is like in the soil and not to determine a specific concentration.

The RIKA and JXCT commercial sensors are provided with a general calibration equation which converts the voltage read between the electrodes into mg per liter. However, for an accuracy enhancement it is usually recommended to perform a soil-moisture specific calibration since this calibration equation has been built based on a standard nitrate liquid solution.

During calibration, three probes of each type were used in order to determine their repeatability and reproducibility. Three repeated measurements were performed in each trial. For the repetition, the probes were not extracted from the soil and reintroduce them again to avoid changing the compaction of the soil. The Gauge Repeatability and Reproducibility (R&R) study was conducted by a one factor Analysis of Variance (ANOVA) test, performed to analyze the variability of data between probes and within a single probe (Tsai, 1988). The one factor considered is the used of three units of each experimental sensor (Figure 12). The ANOVA test was applied only for 35% moisture.

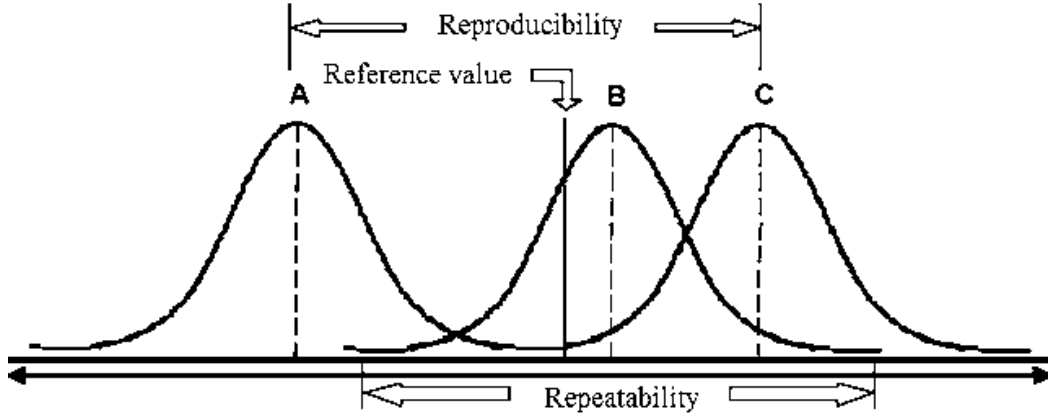


Figure 12. Graphical representation of the concept of repeatability and reproducibility (Source: Barbosa et al., 2014).

Repeatability is the variation of the results of several measurements obtained with successive attempts, with the same sensor and the same laboratory conditions. Reproducibility is the variation in the average of measurements made by different sensors using the same measurement system, measuring the same characteristics under the same conditions. Moreover, variability estimators associated with repeatability and reproducibility have been defined:

$$\sigma_{\text{repeatability}} = \sqrt{MS_{ii}} \quad (3)$$

$$\sigma_{\text{reproducibility}} = \sqrt{\frac{|MS_{ij} - MS_{ii}|}{n}} \quad (4)$$

$$\sigma_{\text{sensor}} = \sqrt{\sigma_{\text{repeatability}}^2 + \sigma_{\text{reproducibility}}^2} \quad (5)$$

$$\% \text{ Repeatability} = 100 \frac{\sigma_{\text{repeatability}}^2}{\sigma_{\text{sensor}}^2} \quad (6)$$

$$\% \text{ Reproducibility} = 100 \frac{\sigma_{\text{reproducibility}}^2}{\sigma_{\text{sensor}}^2} \quad (7)$$

Where $\sigma_{\text{repeatability}}$ and $\sigma_{\text{reproducibility}}$ are the variability estimators corresponding to repeatability and reproducibility respectively, σ_{sensor} is the general variability associated to the sensor, MS_{ii} is the mean square error among the measurements of the same sensor, MS_{ij} is the mean square error among the measurements of the sensors, n is the number of observations and %Repeatability and %Reproducibility are the corresponding percentages of the whole variation associated with repeatability and reproducibility, respectively (Rosenbaum et al., 2010).

4. RESULTS AND DISCUSSION

In this section, the results of the tests explained above are presented and discussed.

4.1 Evaluation of electrical conductivity (EC)

The Figure 13 shows the response of the nitrate reading of the probes with respect to the increase in electrical conductivity in the absence of ion nitrate.

Section a) of the figure represents the behavior of the Nutrisens probe. The results have a range from 225 to 360 mV and have a logarithmic trend, when the EC is low the variability is greater than when it is high. Irrigation water has low electrical conductivity, and the usual range is between 0 and 3 mS/cm (Ayers & Westcot, 1985) also the soil salinity must be taken into account, since it is in the soil solution where the probes are designed to work, it can range from 0 to more than 16 mS/cm for saline soils (USDA, 1954). The probes installed in the soil will experience lower salinity conditions than the ones evaluated in the test. Should be mentioned that these types of sensors are selective but not specific. That is, they are selective, in this case, to nitrate, but if there are ions with similar chemical characteristics, for example chloride, there is some interference. Chloride is the main interferent of this sensor. This interference is more pronounced if the ion to which it is selective is not present in the medium. The trend of the results should be on a decreasing logarithmic scale if they were measuring nitrate, and in this case, it is the opposite, so it is confirmed that they are not measuring nitrate concentration when the EC is increasing.

Section b) of the figure represents the behavior of the JXCT and Rika probes. Three probes of each were analyzed. The results do not follow any pattern. It can be concluded that for low electric conductivity the probes are sensitive and for an EC higher than 40 mS/cm the probes stabilize measuring 208 NO₃⁻ mg per liter. For the salinity range in agronomy these probes are sensitive to EC and the results are not constant between probes nor companies.

The Table 3 shows the determination coefficients of the different probes. The Nutrisens probe presents a perfect fit while the results of the JXCT and Rika probes show their lack of cohesiveness.

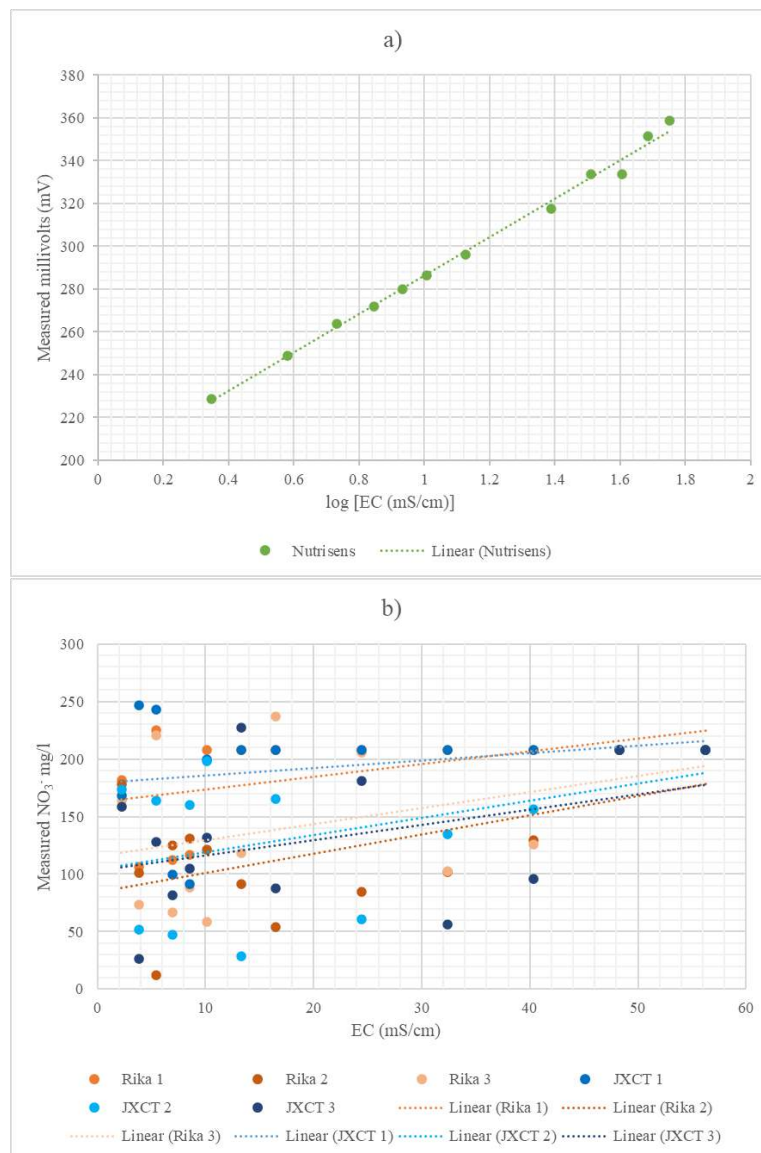


Figure 13. Behavior of the different probes when increasing the electric conductivity.

a) Nutrisens probe b) RIKA and JXCT probes

Table 3. Calibration equations and determination coefficient for the probes when increasing the EC.

	a	b	R^2
SENSORS	$y=ax+b$		
Nutrisens	89.87	196.40	0.99
RIKA	1.10	162.33	0.22
	1.67	84.53	0.29
	1.40	115.53	0.15
JXCT	0.64	179.40	0.06
	1.50	104.24	0.18
	1.33	102.83	0.15

4.2 Evaluation of nitrate concentration in liquid medium

The Table 4 shows the results obtained. Figure 14a represents the Nurisens probe and presents the millivolts measured according to the nitrate ion versus the corresponding reference value (NO_3^- mg/l). As can be seen, the measured data have a decreasing logarithmic adjustment when increasing the nitrate concentration, this is consistent with what is presented in the patent (Alonso & Arasa, 2020). The linear coefficient of determination (R^2) is higher than 0.99 (Table 4). Figure 14b represents the Rika and JXCT probes and presents the measured NO_3^- mg per liter versus the observed or known NO_3^- mg per liter. The linear fit of both probes is close to the theoretical fit (1:1) and their linear coefficient of determination is similar and high around 0.955 (Table 4). All R^2 can be said to be quite good, especially the one of the Nutrisens probe, which is practically 1.

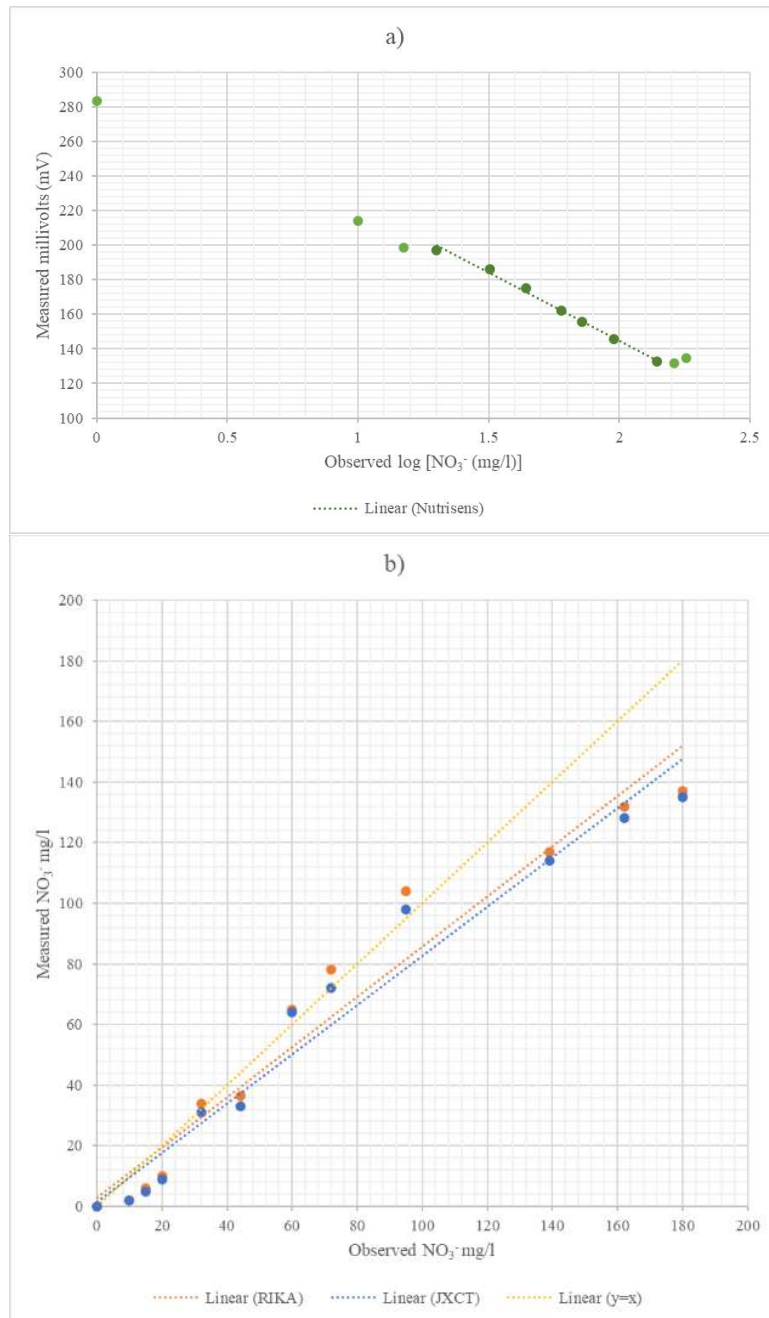


Figure 14. Behavior of the probes at different nitrate concentrations in liquid medium. a) Nutrisens probe b) RIKA and JXCT probes.

Table 4. Calibration equations and determination coefficient for the probes in liquid medium.

	a	b	R ²
SENSORS	y=ax+b		
Nutrisens	-79.24	303.04	0.99
RIKA	0.83	3.05	0.95
JXCT	0.81	1.58	0.96

4.3 Evaluation of nitrate concentration in sandy soil

The data is represented by circles whose interior is colored in a gray scale according to the percentage of moisture of the sample, with white being the lowest (5% moisture) and black the highest (35% moisture).

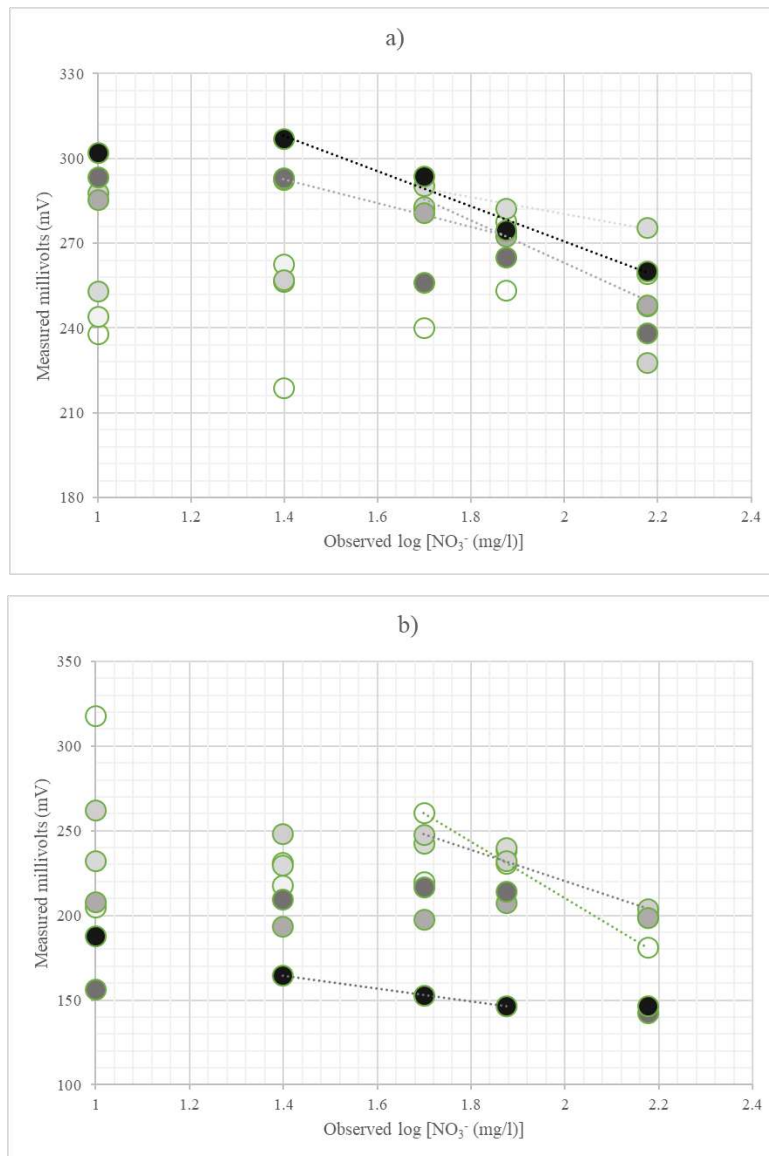
The results of the Nutrisens probes are shown in Figure 15. The millivolts measured for the nitrate ion are presented versus the corresponding reference value in a logarithmic scale (NO_3^- mg/l). As can be seen in the figure, as the concentration of nitrate in the sample increases, the measured millivolts decrease for most of the moisture contents, this is because what is measured is an anion. The moisture content affects the probe readings as can be seen in the figures because the higher the moisture content, the more the dissolution in the soil matrix, the better the reading of the probes.

For linear adjustments of this probe, only the linear part of the reading is considered since the readings of the probes at low concentration are not sensitive. It has been considered linear when there were at least three points with this trend. The Table 5 shows the adjustment only for the tests in which this trend has been observed, for the rest we consider that the readings do not show the trend they should due to, as mentioned before, the reinstallation of the probes that the manufacturer advises against.

Throughout the experiment, it has been observed that the gel covering the sensor has been gradually damaged due to the high number of repetitions carried out during the test. The purpose of the probe is to leave the probe installed in one place. They are not designed to be reinstalled as the membrane can be damaged. This may have influenced the data collection.

These types of potentiometric sensors are supposed to take less than a minute to respond. During the test it was decided to leave them for 5 minutes as there was a variation in the measurement over time. Due to this variation, the behavior of three Nutrisens probes was studied during 24 hours in a sand at 30% humidity and 150 ppm. The probes became stable after approximately 6 hours (Figure 16). Since its stability took much longer than indicated, it is assumed that the reading is interfered with the sand and may be sequestering nitrate. A chemical analysis of the sand would be needed to confirm this.

To study the variability between readings of the same sensor and between sensors, it was proceeded to perform the Gage Reproducibility & Repeatability study using the ANOVA test in Excel. The results were processed to obtain what is in Table 6. All the values are consistent for the different nitrate concentrations. All the P_{values} are smaller than 0.05 which means that there is variability among the three probes for all the readings. The standard deviation of the readings among a single probe (repeatability) is very low since the maximum deviation is 4. The standard deviation among the different probes (reproducibility) is very high, around 90, which causes the standard deviation of the sensor to be very high. The variability among Repeatability and Reproducibility is distributed as a percentage. The results give almost 0% repeatability which indicates that there is hardly any variability between readings from the same probe, which is a positive aspect. On the other hand, 100% is for reproducibility, which indicates that there is a large variability between probes. These results make sense since Nutrisens says that each probe must be analyzed individually as they will not measure the same number of millivolts.



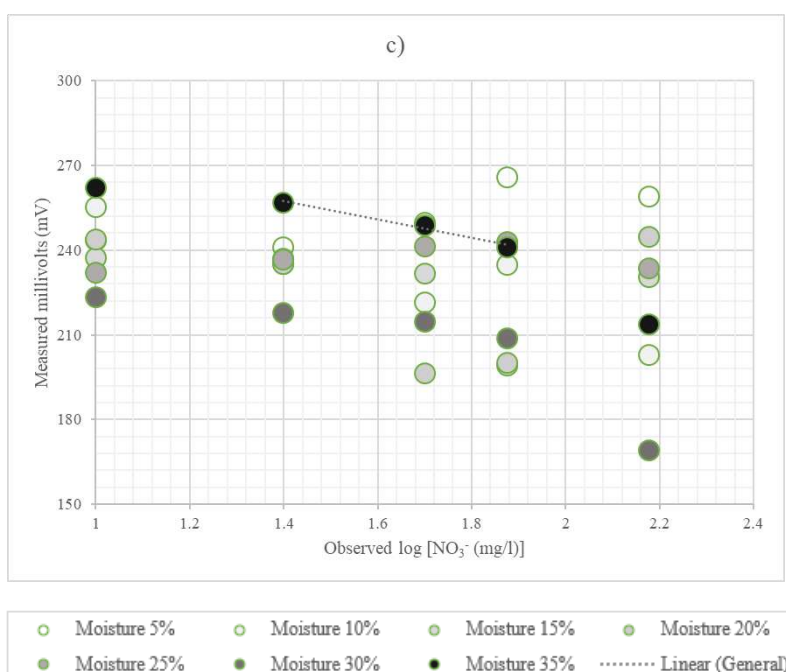


Figure 15. Nutrisens probes behavior at increasing nitrate concentration and different soil moistures. a) Probe 1, b) Probe 2, c) Probe 3.

Table 5. Nutrisens linear calibration equations for the probes in sandy soil ($y=ax+b$).

Moisture %	Probe 1			Probe 2			Probe 3		
	a	b	R ²	a	b	R ²	a	b	R ²
5				-165.86	542.07	1			
10	-74.86	412.75	0.94						
15	-30.16	340.62	0.97						
20				-91.50	403.36	1			
25	-41.53	350.67	1						
30									
35	-62.44	395.51	0.97	-37.54	216.94	1	-32.47	302.83	0.98

Table 6. Gauge R&R study for Nutrisens probes.

NO ₃ ⁻	P _{value}	σ Repeatability	σ Reproducibility	σ Sensor	% Repeatability	% Reproducibility
10	5.770E-10	4.110	82.176	82.278	0.25	99.75
25	8.923E-13	1.736	102.134	102.149	0.03	99.97
50	1.715E-16	0.416	101.973	101.974	0.00	100.00
75	3.499E-18	0.200	93.715	93.715	0.00	100.00
150	4.404E-14	0.833	80.895	80.899	0.01	99.99

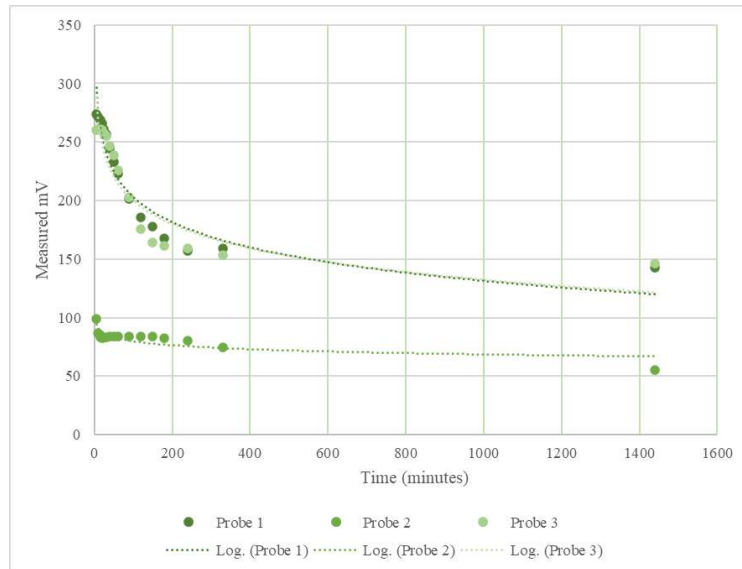


Figure 16. Nutrisens probes behavior at 30% moisture and 150 NO_3^- mg/l.

The results of the RIKA and JXCT probes are represented in Figure 17 and

Figure 18. As both companies have the same type of sensor, the results will be analyzed together. The observed nitrate concentration is represented versus the measured nitrate concentration. Observing the two figures, all the results have the same trend. When the nitrate concentration increases, the readings increase as well as with increasing humidity. Readings with moistures from 5% to 20% have less sensitivity than those from 25% to 35%. This can also be seen in the Table 7 and Table 8, where the term a from the function indicates the slope of the linear fit. The smaller the value of the slope means that there is less variability between the results. Overall, as humidity increases, the slope of the linear regression increases although the values are far from the theoretical slope which in this case is 1 ($y=x$).

From the behavior of these sensors in sand it can be concluded that as the nitrate concentration and humidity increase, they measure better but are far from the theoretical reading. With a calibration equation the results would improve but these probes are not very sensitive to nitrate variability since the slope of the linear regression is very slight.

To study the variability between readings of the same sensor and between sensors, it was proceeded to perform the Gage R&R study using the ANOVA test in Excel.

The study of variability between readings of the same sensor and between sensors using the ANOVA test was impossible to perform for these probes because there is no variability among readings of the same probe. This means that all the variability is caused by the different probes. Observing the Figure 17 and

Figure 18 the measured values are around the same interval but there are some variabilities. For these probes it is also recommended to calibrate them individually, even though the manufacturer does not indicate anything about recalibrating the probes.

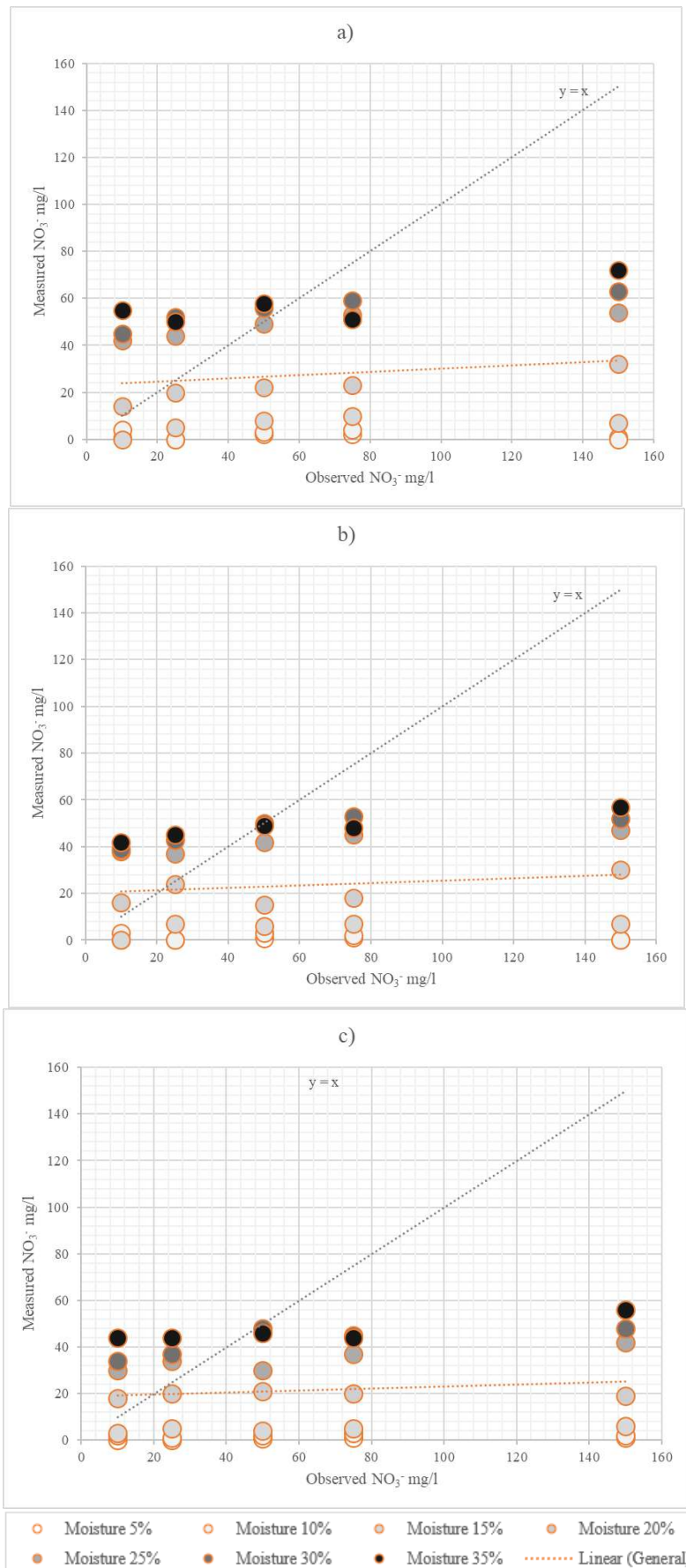


Figure 17. RIKA probes behavior at increasing nitrate concentration and different soil moistures. a) Probe 1, b) Probe 2, c) Probe 3.

Table 7. RKA linear calibration equations for the probes in sandy soil ($y=ax+b$).

Moisture %	Probe 1			Probe 2			Probe 3		
	a	b	R ²	a	b	R ²	a	b	R ²
5	0.0046	0.8505	0.0835	0.0004	0.3078	0.0023	0.0077	0.058	0.6975
10	-0.0158	3.1814	0.1809	-0.0137	2.4485	0.2469	0.0041	1.7444	0.1031
15	0.0383	3.6232	0.3073	0.031	3.4782	0.3133	0.0168	3.5573	0.6598
20	0.114	15.131	0.9341	0.0803	15.622	0.4913	0.0003	19.58	0.0003
25	0.0858	43.079	0.7892	0.0719	37.343	0.8381	0.0824	29.494	0.7972
30	0.1134	47.972	0.8203	0.0862	42.054	0.6046	0.0904	36.798	0.5853
35	0.1313	49.058	0.6646	0.0992	42.051	0.9409	0.0851	41.525	0.807
General	0.0674	23.271	0.0189	0.0508	20.472	0.0147	0.041	18.965	0.0117

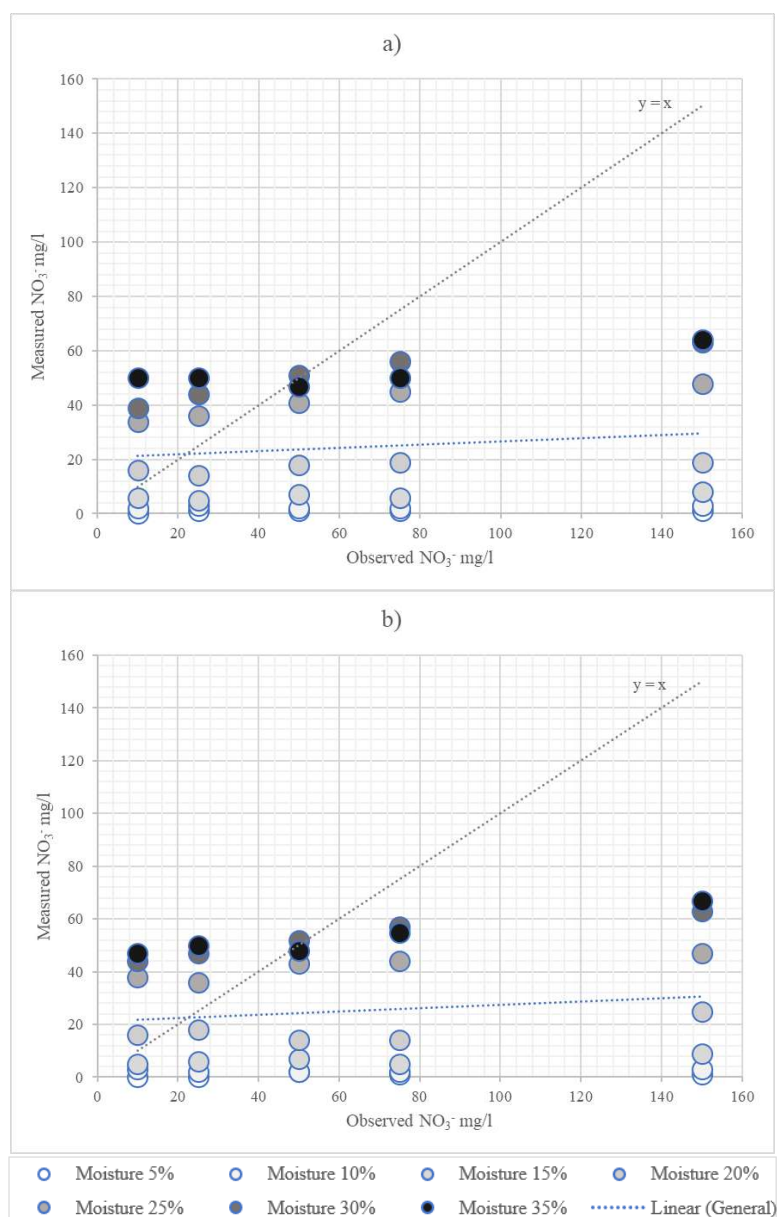


Figure 18. JXCT probes behavior at increasing nitrate concentration and different soil moistures. a) Probe 1, b) Probe 2, c) Probe 3.

Table 8. JXCT linear calibration equations for the probes in sandy soil ($y=ax+b$).

	Probe 1			Probe 2		
Moisture %	a	b	R ²	a	b	R ²
5	0.0043	0.5342	0.2786	0.0063	0.4064	0.1746
10	0.0042	2.1393	0.1787	0.003	2.216	0.089
15	0.0166	5.3726	0.6405	0.024	4.9126	0.6233
20	0.0291	15.396	0.5464	0.059	13.74	0.508
25	0.1003	34.58	0.8797	0.0729	37.082	0.7934
30	0.1652	40.357	0.9166	0.1347	44.248	0.9439
35	0.1045	45.719	0.7331	0.1435	44.501	0.9282
General	0.0606	20.585	0.019	0.0633	21.015	0.0196

5. CONCLUSION

In this work, the behavior of several probes corresponding to three companies has been studied under the same conditions.

First, the susceptibility of the probes to electrical conductivity was studied. The Nutrisens probe has an opposite behavior of the millivolt measurement for nitrate ion for an increasing EC than for an increasing nitrate concentration. This sensor is ion selective but not specific and chlorine is the main interference ion being more significant in the absence of nitrate. It has a variability of 130 mV from 0 to 55 mS/cm. The RIKA and JXCT probes do not follow any pattern when the EC is low. Each probe gives a different reading from the other probes, they are unstable and chaotic.

Then, the behavior of the probes were studied in a liquid medium at different nitrate concentrations. In this test, the Nutrisens probe fits a logarithmic regression with an R^2 greater than 0.99. The RIKA and JXCT probes adopt a linear regression where their R^2 are 0.95 and 0.96 respectively. It can be concluded that all three probes perform well in liquid media, emphasizing the Nutrisens probe. It is remarkable that the Chinese probes have been calibrated by the manufacturer in solution where they respond quite well.

Finally, the behavior of the probes were studied in a sandy soil, at different volumetric humidities and nitrate concentrations. In this test, the Nutrisens probes show that they have a millivolt reading with a negative logarithmic trend as the nitrate concentration increases. This is true for all moistures except the lowest, 5%. These probes are valid for monitoring nitrate trends in the soil although the readings will also be affected by the amount of moisture in the soil. The RIKA and JXCT probes adopt a linear regression for each moisture content. Both probes show little or no sensitivity when humidity is low. As the moisture content increases, the readings become closer to the actual readings. The sensitivity of these probes is very low since the slope of the linear regressions range from 0 to 0.16 (increasing value as humidity increases) when the theoretical is 1.

No cross effects with other macronutrients, such as potassium or phosphorus, have been analyzed. It is to be expected that in the Chinese probes, as seen in the EC study, the readings are affected, since the calibration equation is given for a standard liquid solution of NO_3 , without the presence of other elements. As it has been observed throughout the study, all the probes are affected by the amount of moisture in the soil, so it would be convenient to perform a multiple linear regression since it depends on two variables, nitrate concentration and moisture. In addition, it would be of great value to be able to extend the study to another type of sand, with a different composition, to analyze the cross-matrix effects.

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APPENDIXES

Appendix 1: JXCT manufacturer calibration certificate

	深圳中电计量测试技术有限公司 Shenzhen Zhongdian Metrology and Testing Technology Co., Ltd			中国认可 国际互认 校准 CALIBRATION CNAS L10486
校准证书 CALIBRATION CERTIFICATE				
		第 1 页, 共 3 页 Page of		
证书编号 Certificate No.	ZD202109014221			
委托方 Client	威海精讯畅通电子科技有限公司			
委托方地址 Address	山东省威海市环翠区火炬高技术产业开发区火炬路221号			
仪器名称 Description	土壤氮磷钾传感器			
型号规格 Model/Type	JXBS-3001-NPK			
制造厂 Manufacturer	威海精讯畅通电子科技有限公司			
出厂编号 Serial No.	/	管理编号 Asset No.	JX-CGQ-001	
样品接收日期 Date of Receipt	2021-09-01			
校准日期 Date of Calibration	2021-09-01			
批准人 : Approved Signatory	王小龙			
审核 : Inspected by	梁圣学			
校准 : Tested by	郑世陈			
校准专用章 (stamp)				
				
地址 : 广东省深圳市宝安区福永街道白石厦社区东区新开发区4栋301 Add : Room 301, Building 4, New Development Area, East Zone, Baishixia Community, Fuyong Sub-District, Bao'an District, Shenzhen, Guangdong, China 电话 (Tel) : 0755-29888158 邮政编码 (Post Code) : 518103 传真 (Fax) : 0755-29796107				



深圳中电计量测试技术有限公司

Shenzhen Zhongdian Metrology and Testing Technology Co., Ltd

校准说明

DIRECTIONS OF CALIBRATION

证书编号: ZD202109014221

Certificate No.

第 2 页, 共 3 页

Page of

1. 本实验室出具的数据均可溯源至国家计量基准。
(All data issued by ZD Test are traced to National Primary Standards.)
2. 本结果仅对当次被测样品有效, 如有疑问请在15个工作日反馈。
(The results is ONLY valid for the tested sample, please feedback to us within 15 working days if you have any question.)
3. 本证书编号具有唯一性, 若替换证书, 自发出后原证书即可作废。
(Each certificate has a unique number. If replaced the certificate, the original certificate will be invalid once the new certificate number is issued.)
4. 证书中如有最大允许误差、判定结果, 仅供参考, 其中“P”代表“Pass”, “F”代表“Fail”。
(In the datasheet, MPE & determination is only for reference, "P" represents "Pass" and "F" represents "Fail".)
5. 本次校准的技术依据及获认可的能力范围, 超出范围的内容未被认可。
(Reference documents and Accredited Scopes for Calibration, Beyond the Scope has not been accredited.)

01 《技术说明》

6. 本次校准使用的主要测量标准 (Main Standards of Measurement Used in the Calibration.):

名称/型号 Description/Model	编号 Serial No.	证书号 Certificate No.	有效期至 Due Date	技术特征 Technique Character
二等标准密度计	/	HCM201801548	2021-12-24	修正值: $U=0.00015\text{g/cm}^3$ $k=2$
氮含量测定用标准物质		GBW(E)060111	2022-06-15	/

7. 校准地点、环境条件 (Place and environmental conditions of the calibration)

地点 Place	本公司实验室	温度 Temperature	23.5 °C	相对湿度 Relative Humidity	55 %
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8. 建议复校时间间隔:

Suggested calibration interval is

12 个月, 送检单位可根据实际情况自主决定。
12 month or it can be altered depending on the actual usage of the user.



深圳中电计量测试技术有限公司

Shenzhen Zhongdian Metrology and Testing Technology Co., Ltd

校准结果

Result of Calibration

证书编号: ZD202109014221
Certificate No.

第 3 页, 共 3 页
Page of

1、外观及各部分功能相互作用:

In view of externa and the function of each part of interaction:

正常

2、示值误差的校准:

Normal

Calibration of indication error:

标称值	实测值	修正值	不确定度
Nominal value	Measured value	Correction value	Uncertainty
(mg/kg)	(mg/kg)	(mg/kg)	$U(k=2)$ (mg/kg)
500.00	501.00	1.00	0.2
1000.00	1002.00	2.00	0.2
1900.00	1902.00	2.00	0.2

备注:

Notes:

1. 依据(Reference document)

JJF 1059.1-2012 测量不确定度评定与表示

(JJF 1059.1-2012 Evaluation and Expression of Uncertainty in Measurement)

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