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Article

Development of a Novel Nitrate Portable Measurement System Based on UV Paired Diode–Photodiode

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Abstract: Nitrates can cause severe ecological imbalances in aquatic ecosystems, with considerable consequences for human health. Therefore, monitoring this inorganic form of nitrogen becomes essential for any water quality management structure. This research aimed at developing a novel Nitrate Portable Measurement System (NPMS) for monitoring nitrate concentrations in water samples. NPMS is a reagent-free ultraviolet system developed using low-cost electronic components. Its operation principle is based on Beer-Lambert law for measuring Nitrate concentrations in water samples through light absorption in the spectral range 295-315 nm. The system is equipped with ready to use ultraviolet sensor, Light Emission Diode (LED), op-amp, microcontroller, liquid crystal display, quartz cuvette, temperature sensor, and battery. All the components are assembled in a 3D-printed enclosure box which allows a very compact self-contained equipment, with high portability, enabling field and near real time measurements. The proposed methodology and the developed instrument were used to analyse multiple nitrate standard solutions. The performance was evaluated in comparison with the Nicolet Evolution 300, a classical UV-Vis spectrophotometer. The results demonstrate a strong correlation between the retrieved measurements by both instruments within the investigated spectral band and for concentrations above 5 mg NO₃⁻ /L.

Keywords: nitrate; UV; optical; spectroscopy; real time; portable device; water; absorbance; opto-electronic; chemistry; environment; human health

1. Introduction

Monitoring aquatic systems play a crucial role in managing water used for human consumption, aquaculture, recreational activities, irrigation, and industrial processes [1,2]. Nitrates (NO₃⁻) are a common contaminant of surface waters [3–5]; therefore, they can pose severe risks to the environment [6,7] and human health [8–10]. Excessive amounts of NO₃⁻ in water bodies may increase the risk of aquatic environment degradation such as eutrophication, resulting in the rapid growth of harmful

algae blooms [11], cyanobacteria [12], bottom anoxia [13], and can lead to an increase of methane levels in the atmosphere [14,15]. Drinking water contaminated by NO_3^- is also correlated with fetal malformations during the pregnancy [16,17], development of new-born methemoglobinemia [18,19], and may increase the risk of colorectal cancer related to the transformation of NO_3^- into N-nitroso carcinogenic compounds [20,21]. The 91/676/EEC (Nitrate Directive), concerning the protection of waters against pollution caused by NO_3^- from agricultural sources [22], transposed by Decree-Law 235/97 [23], defines an admissible concentration level of 50 mg NO_3^-/l in freshwater for human consumption. The target 6.3 water quality and wastewater from the United Nations Organization sets the objective for 2030 concerning the improvement of water quality to protect ecosystems and human health [24,25]. The same target refers to the monitoring as a key tool for the policy- and decision-makers to identify the water bodies with high concentration of pollutants. An affordable device for water NO_3^- determination can also help developing countries to ensure availability and sustainable management of water and sanitation for all [24].

There exist several laboratorial methods available that are used for the determination of NO_3^- in drinking water such as: the spectrophotometry in the ultraviolet (UV) spectral region at 220 nm [26,27], the second derivative of UV spectrum [28,29], the ultraviolet screening [30], the NO_3^- electrode [31], the cadmium [32] and hydrazine reduction [33] and finally the cadmium reduction flow injection [34]. Although these methods are precise and accurate, they pose some disadvantages: requiring intensive time and laborious techniques [35], relying on expensive equipment [36], needing to be operated in the laboratory, and depending on the use of chemical reagents in colorimetric procedures. They also require the transportation of the samples to the laboratory which can increase the risk of contamination by mineralization, nitrification/denitrification, fluctuations of the temperature, and container handling [37,38]. In order to overtake these constraints, portable devices can be used directly in the field.

Portable spectral integrating devices can be used to quantify the absorbed radiation of the chemical compounds by varying the impedance or by converting the captured radiation into an electrical signal [39,40]. Several studies reported and quantified the presence of NO_3^- in agricultural nutrient determination and wastewater and organic compounds using as proxy its typical absorption peak at 302 nm [41,42]. Traditionally this peak is also used in the food industry for high concentrations typically above 1000 mg NO_3^-/l because of the high linearity between the absorbance and the level of NO_3^- present in the sample and the unnecessary use of reagents [43]. For lower concentrations the $n \rightarrow \pi^*$ weak absorption band of the NO_3^- around 302 nm is far more challenging than using the traditional 220 nm NO_3^- absorbance peak due to the lower absorbance as reported in [44]. The band between 295 and 300 nm have been used by some authors to correct the absorbance measured at 220 nm when a higher concentration of dissolved organic matter is present on the water sample [45]. Besides, this peak (302 nm) is not subjected to major wavelength shifts as the concentration increases [46,47] responsible for an increased error in the measurement of the NO_3^- concentration. Additionally, the UV LED introduced in this work presents a significantly lower commercial cost [48] compared to others UV LED near the 220 nm on the market [49].

Moo et al [48] as well as Szolga and Cilean, [49] have applied a similar methodology for the determination of nitrate in water samples at wavelength of 302 nm. However, the authors employed light sources that were not sufficiently optimized, and they also used photodetectors with large detection windows lacking filters to eliminate unwanted interferences. Additionally, some have also used principal components analysis (PCA) to derive more than one parameter from the mixture without prior separation. They were unable to accurately determine the amount of NO_3^- presented in the samples for concentrations below 50 mg NO_3^-/l , as required by the European Nitrate Directive [22,50], the Nitrate Pollution Prevention Regulations Implementation of the Nitrates from the United Kingdom [51] and the National Primary Drinking Water Regulations from United States regulations [52]. Ingles et al. [53] developed a low-cost smartphone approach to determine the level of NO_3^- in water samples. The instrument implies the usage of a scintillator to convert the UV light into a visible green light and uses a setup based on a smartphone to record and process the signal. They describe it as a simpler, a more compact and less expensive system than the typical laboratory spectrometer.

This study presents the development and calibration of a new optical device called Nitrate Portable Monitoring System (NPMS) based on low-cost optical and electronic components with high accurate spectral characterization for NO_3^- determination in water. The uncertainties associated with the low-cost UV light-emitting diode (LED) were determined following the methodology outlined in Silva et al. [54] to assess the probability distribution, the corresponding peak radiation wavelength, the standard deviation and its suitability for use in NO_3^- measurements.

The design of the sensing system, its description in term of hardware components as well as the characterization of the different optical and electronic parts and the processing techniques are presented in section 2. Section 3 deals with the calibration of the developed NPMS, and the performance comparison towards a bench top laboratory spectrometer using a batch of NO_3^- standard samples prepared in laboratory. The best fitting process and data analysis are presented as well as the evaluation of the uncertainties for both instruments. The last section discusses the obtained results, highlighting the peculiar features of the NPMS and the expected future activities.

2. Materials and Methods

2.1. Instrument Description

A conceptual diagram showcasing the paired diode-photodiode NPMS is presented in (Figure 1). This diagram is divided into three subsystems: i) photon source module, which provides the radiation within the wavelengths range of NO_3^- spectral absorption; ii) sample support module that accommodates the quartz cuvette containing the water sample to be analysed and isolating the sample from the outside radiation to reduce possible interferences; iii) processing and sensing module, where the spectra acquisition takes place, along with the implemented algorithm to determine the stability of the recorded signal and to retrieve the NO_3^- concentration displayed on the integrated LCD display. A computer can also be connected to the system to store the values in a permanent memory.

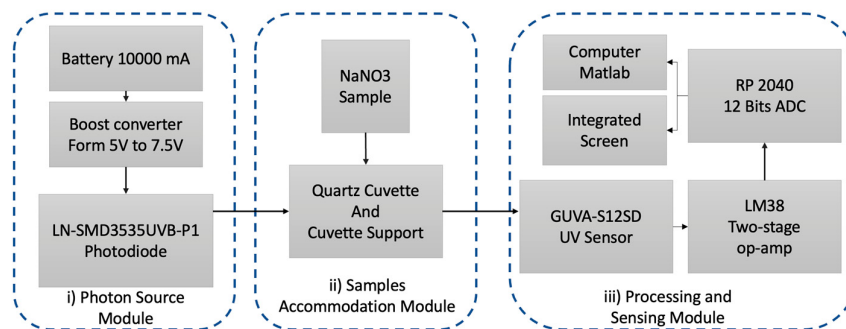


Figure 1. Block diagram of the nitrate measurement system with main of the developed NPMS and their interactions.

2.2. Photon Source

The instrument was developed taking into account the emission spectra of the LN-SMD3535UVB-P1 diode due to the characteristic emission radiation matching the absorption peak of NO_3^- at 302 nm. The LED presents a spectral range between 295 and 315 nm with a peak at 308 nm. The diode is powered with a 7.5 V from and interfaced with a 60 Ω load resistance as shown in Figure 2, where the arrows indicate the radiation direction. To reduce the noise associated with the environment and to minimize the distance from the sensor, the diode was mounted at the entrance of the cuvette support.

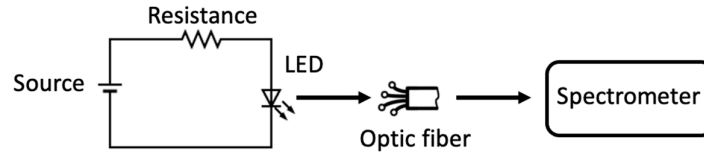


Figure 2. Light emission diode measurement scheme.

Aiming to characterize the LED, its spectrum was acquired 5000 times using the SNT-BLK-CXR UV-Vis spectrometer through an optic fiber as depicted in Figure 2. The carried out measurements allowed to verify the device stability, statistical distribution and parameter estimation. The Chi-Square test was applied to the recorded spectra to assess whether the radiation emitted by the LED follows a normal distribution. The spectral radiation intensity distribution showed a peak intensity at 308 nm within the range from 285 to 900 nm, as depicted in Figure 3.

The observed emission range from the LED was between 295 and 315 nm. Maximum and minimum intensity of 60266 and 59998 counts respectively were recorded. Spectral data are presented in digital counts being the output of the spectrometer analog-to-digital converter, and for the LED characterization there is no need to convert it in radiation unity. The spectrometer was operated with an integration time of 57 milliseconds.

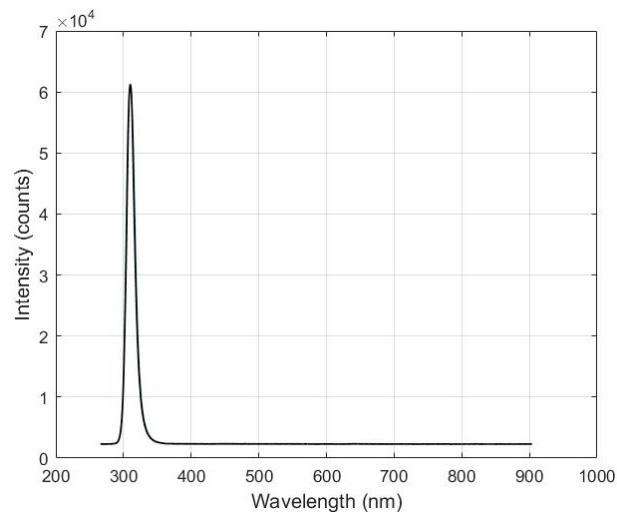


Figure 3. Spectral energy distribution of the LN-SMD3535UVB-P1 LED with peak emission at 308 nm.

The frequency distribution of the LED emitted intensity (blue bars) and the respective Gaussian distribution function (red curve) are presented in (Figure-4). The Chi-Square test determined that the upcoming radiation from the LED follows a normal distribution for a p-value of 0.5. The reading of the average intensity was 60112 counts with a standard deviation of ± 40 counts. Several tests have been carried out in order to verify the reliability of the measurements.

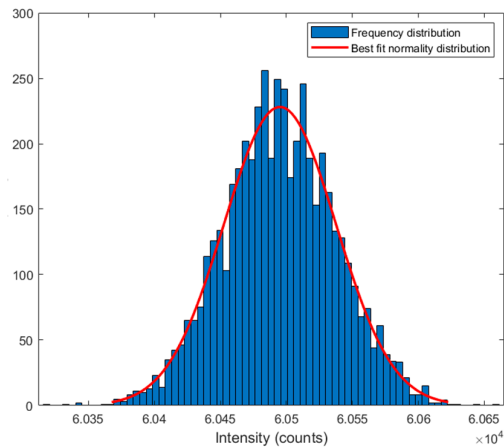


Figure 4. Histogram of the normal distribution of the 308 nm peak for 1000 measurements.

2.3. Processing and Sensing System Design

The developed standalone device for the detection of NO₃⁻ is based on a sensing system that is composed primarily of the GUV A-S12SD UV sensor [55]. The main function of the probe is to convert the incoming radiation emitted by the diode into an electrical signal to be processed by the microcontroller. The sensor is a low-cost UV Schottky-type photodiode with gallium nitride-based material, and it is usually applied for the detection stage [49]. The spectral response covers the UVA and part of the UVB range from 240 to 370 nm. The main features of the photodiode are reported in the Table 1.

Table 1. Photodiode electrical characteristics.

Parameter	Value
Forward current	1 mA
Reverse voltage	5 V
Working voltage	2.7 V to 5.5 V
Active area	0.076 mm ²
Typical dark current at 25 °C with VR of 0.1V	1 nA
Photocurrent with UVA Lamp of 1 mW/cm2	113 nA
Temperature coefficient	0.08 %/°C
Responsivity at λ = 300 nm with VR of 0V	0.14 A/W
Operation temperature	-30 °C to 85 °C
Spectral detection range	240 to 370 nm

Due to the low light intensity produced by the LN-SMD3535UVB-P1 LED and low absorbance of the NO₃⁻ at 302 nm, the built-in sensor op-amp SGM8521 [56] was combined with the LM358 op-amp in a two-stage configuration. This amplifier can be supplied with a voltage ranging from 3.5 to 24 V, it has a maximum electric DC current output of 20 mA and a gain of 1000 with the two-stage combined. The schematic illustration for the single beam UV radiation, the quartz cell for water sampling and the sensing module coupled with the op-amp is presented in (Figure-5).

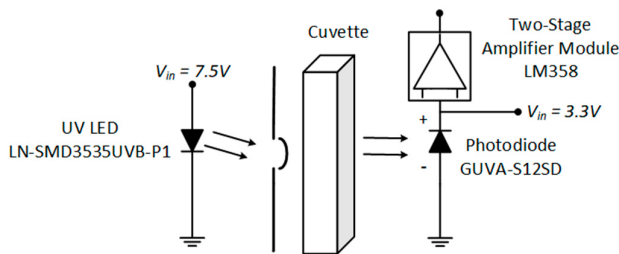


Figure 5. Schematic diagram of the instrument for emission radiation, quartz cell, photodiode and the two-stage amplifier module.

The spectral response of the sensor was reduced to the range of the diode, highlighted with the blue dashed line (Figure 6 (a)), isolating the sensor from the outside environment, to match the diode spectral response line red curve and the NO_3^- peak. In (Figure 6 (b)) is presented the linear response of the sensor for UV-A optical radiation.

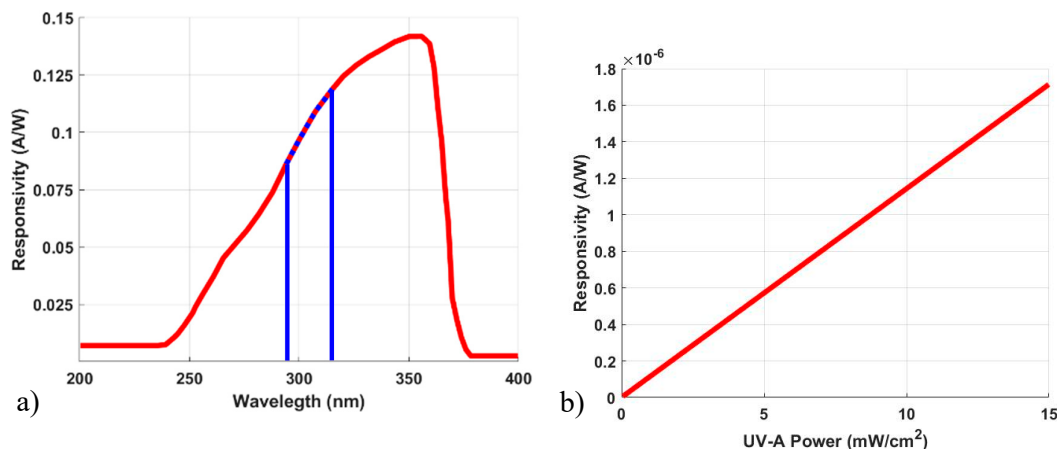


Figure 6. (a) UV sensor response at intensity radiation between 240 and 370 nm (red line) and the diode range emission (dashed blue line); (b) Sensor photocurrent response when irradiated with UV-A radiation [55].

A Raspberry-Pi microcontroller, model RP2040 [57] was adopted for data acquisition and digital processing. The microcontroller architecture is based on dual Cortex M0+ processor cores, up to 133 MHz, a 264kB of embedded SRAM in 6 banks, 30 multifunction GPIO, 2 SPI controllers, 4 multiplex channel 12-bit ADC with a sampling frequency of 500 kHz, and a 1.1 USB host/device. The MicroPython Pycharm interface was adopted for signal acquisition and data processing.

2.4. Enclosure Box and Printed Circuit Board

The electronic components above described are positioned in the specially developed PCB which is contained in a box designed in SolidWorks and 3D printed using black polylactic acid (PLA) filament. The black color of the filament intends to maximize the absorption of the scattered radiation inside the box. The various parts of the NPMS case are highlighted in the (Figure-7(a)), namely: the upper cover (1), the cap to cover cuvette on the cell support (2), the cell support (3), the battery housing (4), the front cover (5) the PCB and electronic components seat in (6) and the LED placed at 1.75 cm from the bottom of the cuvette in the cut-out (7) horizontally aligned with the photodiode.

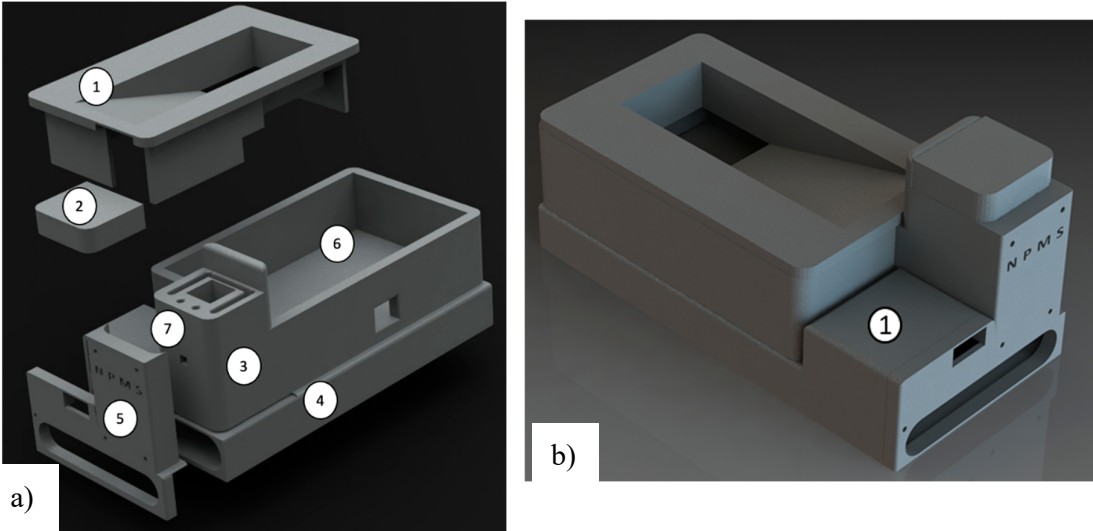


Figure 7. **a)** Exploded view of the 3D model case developed in SolidWorks that accommodate all the NPMS components; **b)** Rendering of the NPMS case assembled.

All electronic components of the device were assembled on a simple 2 sided PCB, as shown in (Figure 8 (a)). The LCD screen is plugged in the screen connector (1), the Raspberry Pi Pico is surface-mounted on pad (2), the two-stage connector is used for the op-amp (3), the UV sensor is connected to (4), and the temperature and humidity sensor is connected at pad (5). Figure 8 (b) shows a photo of the physical PCB, which was produced using FR-4 TG 130-140 material, has a thickness of 1.6 mm, and features a black solder mask.

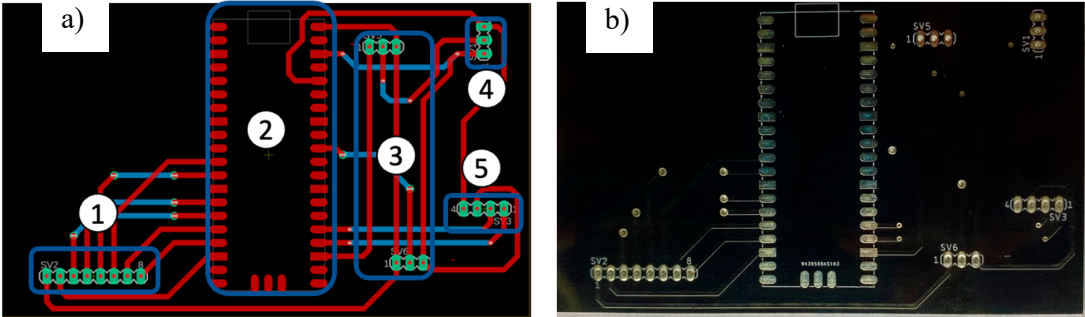


Figure 8. **a)** Diagram of the top side of the printed circuit board, showing the component orientations. In this diagram, the blue lines indicate the vias placed on the bottom surface of the board, while the red lines indicate the vias placed on the top surface. **b)** PCB ready to assemble the electronic components.

The assembled enclosure box in different views is presented in (Figure 9). The top view of the instrument working in standalone mode is show in Figure 9a. The different components can be easily identified: the LCD Module (1), the Raspberry-Pi microcontroller (2), the LM358 Two-stage op-amp (3), the GUVA-S12SD UV sensor (4), the AHT10 humidity, temperature sensor (5), the quartz cell for water samples (6) and the LED housed over the front cover (7). In figure-9b is presented the front view of the instrument displaying the power source connectors for charging and powering purposes. A general upper view of the instrument is shown in Figure 9c. Finally, the lateral view (Figure 9d) allows to identify the engraved entry in the center for the USB connection (1).

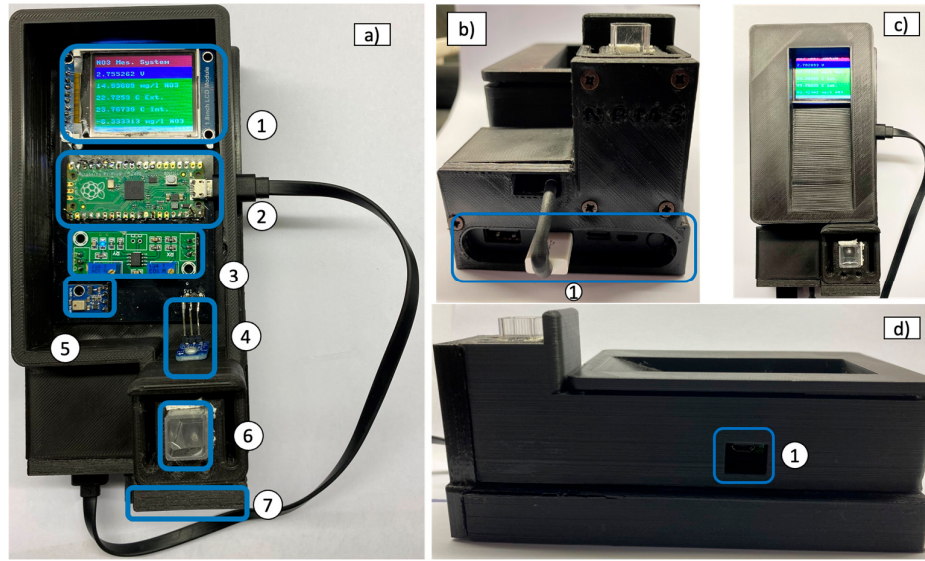


Figure 9. a) Top view of the device NPMS configured for standalone use, b) front view of the instrument, c) Top view of the device fully assembled, d) lateral view of the instrument.

2.5. Samples: Nitrate Standard Solutions Preparation

The standard solutions used to obtain the calibration samples were prepared with the ultrapure water Milli-Q and NaNO₃- Alfa Aesar, 99.0% minimum purity crystalline. Previously decontaminated labware was used. Six different standard solutions of 5, 10, 25, 50, 75, and 100 mg NO₃⁻ /l were prepared to cover a wide range of concentrations below and above the regulation limits. The mass of NaNO₃ for the solutions was obtained from stoichiometry calculations.

From the stock solution, the adequate volumes were extracted and diluted to 100 ml with ultrapure water to prepare the standard solutions of interest. From the stock solution, the amounts of 10, 7.5, 5, 2.5, 1, and 0.5 ml were extracted and diluted to 100 ml with ultrapure water to prepare the standard solutions of interest. To prevent the degradation of the NO₃⁻ samples throughout the experiment, all the solutions were stored below 2 °C.

2.6. Calibration Algorithm

The methodology for the NPMS calibration foresees the double measurements of the blank sample containing only ultrapure water (I_0) with each one of the samples with different NO₃⁻ concentrations (I_k). The sensor output is measured 24.000 times aiming to reduce the signal-to-noise ratio (SNR) and therefore to obtain results with a better accuracy. For each acquired dataset, the voltage value produced by the UV sensor is proportional to the intensity of the radiation that passes through the water sample. This voltage is read by the ADC of the microcontroller, the signals being filtered using the following algorithm: A Chi-Square test is applied to prevent the acquisition of random or aberrant signals. In this step, if the null hypothesis h_0 is rejected, the collected measurement is also rejected. A simple running average is applied to smooth the acquired signal as Equation 1.

$$\begin{cases} s_1 = \frac{1}{n} \sum_{j=1}^n a_j \\ s_i = \frac{1}{2n} \sum_{j=n(i-2)+1}^{i \times n} a_j \end{cases} \quad (1)$$

with n equal to 6000, i varies between $\{2, \dots, 4\}$, a_j is the measured data set inside each section and S_i is the moving average of each section. Then the initial intensity I_0 and the sample intensity I_k are calculated as the average of $\{S_i\}_{i=1}^4$. The fragmentation of the dataset in multiples intervals (4) is due

to hardware restrictions since this method allows to bypass the memory ram limitation of the RP2040 microcontroller and to increase the number of measurements available for the noise filtering process.

Then, the absorbance is calculated using the following expression

$$I_k(\lambda) = I_0(\lambda) \exp(-\sigma(\lambda)cL) \Rightarrow A = -\log\left(\frac{I_k(\lambda)}{I_0(\lambda)}\right) \quad k=1,2,\dots,6 \quad (2)$$

where I_k denotes the radiation intensity of the beam after passing through the water sample, I_0 is the initial intensity of the blank sample which includes the cell and ultra-pure water, A is the absorbance, σ is the molar absorptivity, λ the wavelength, c the molar concentration of the substance, and L the length of the light path. The UV sensor produce an analogue value (in mV) that is converted in digital counts from the AD converter on the microcontroller. Since this is integrated over the spectral range considered (295-315nm), the digital signal (DS) obtained from the AD is converted in voltage (Vs) using the following relation:

$$V = DS * 3.3 / 2^{ADC_{BN}} \quad (3)$$

where 3.3 is the reference voltage and ADC_{BN} the number of bit of the ADC (in our case $ADC_{BN} = 12$).

Using voltage levels recorded from the UV-sensor, the absorbance A is:

$$A = -\log\left(\frac{I_k(\lambda)}{I_0(\lambda)}\right) = \log\left(\frac{V_{BS}}{V_{NS}}\right) \quad (4)$$

where V_{BS} is the measured voltage of the blank sample using ultrapure water and the V_{NS} is the measured voltage of the water samples containing NO_3^- . To obtain the result of the absorbance per sample a simple average is applied to the acquired signal. Further the absorbance results are stored in a table file. The flowchart in (Figure 10) presents the developed methodology for the process of calibration of the NPMS.

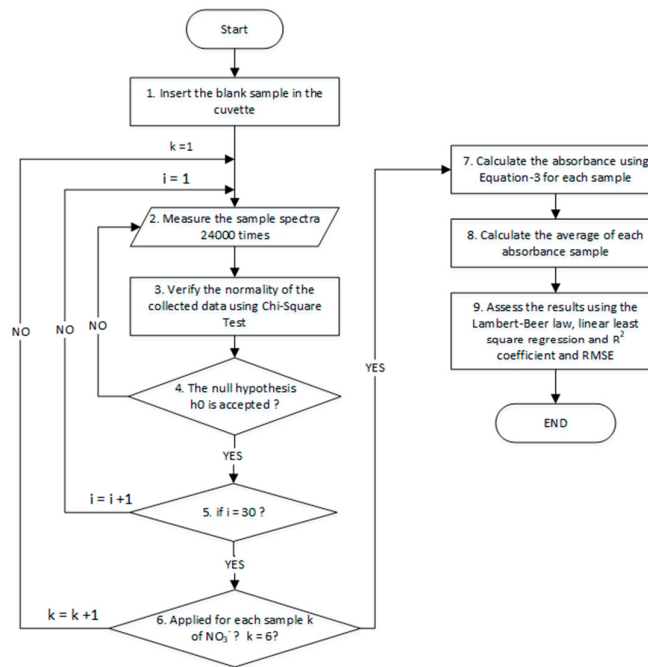


Figure 10. Flowchart for the measurement methodology using the NPMS.

In order to produce the calibration equation for the determination of NO_3^- , the absorbance data is correlated to the known concentration of the standard solutions following Lambert-Beer Law [58], according to the following equation:

$$A = -\sigma(\lambda) c L \quad (5)$$

The best fit function for the measured data is obtained with a linear regression as presented in equation below:

$$Y = \beta X + \varepsilon \quad (6)$$

where Y represents the vector of the measured concentration, X is the matrix of the measured absorbance, ε the error of the estimative and β is the vector of parameters of the linear model to be estimated, which is expressed in Equation 7 and Equation 8.

$$X = \begin{pmatrix} 1 & A_1 \\ \vdots & \vdots \\ 1 & n \end{pmatrix} \text{ with } n = 6; \quad (7)$$

$$\beta = \begin{pmatrix} \beta_0 \\ \beta_1 \end{pmatrix} \quad (8)$$

The linear regression model was estimated using the ordinary least squares method. This approach relies on minimizing the sum of the squares residuals and allows the estimation of the vector of parameters β . The solution β for the linear least-squares fit is:

$$\beta = [X^T X]^{-1} X^T Y \quad (9)$$

2.7. Processing Algorithm for Standalone Measurements

The determination of NO_3 in water samples is performed with the following procedure. First, a blank sample comprising ultrapure water is placed in the cuvette support to establish the necessary instrument offset. Subsequently, the algorithm follows the same procedure as that adopted for the NPMS calibration. The absorbance of the sample is determined using Equation 4, and the NO_3^- concentration in the individual sample is calculated via interpolation of the linear equation derived during the calibration process. The result is then displayed on the integrated LCD screen. Consequently, there is no requirement to connect a PC to the instrument, facilitating on-field measurements. The flowchart outlining this procedure, including the algorithm, is depicted in Figure 11.

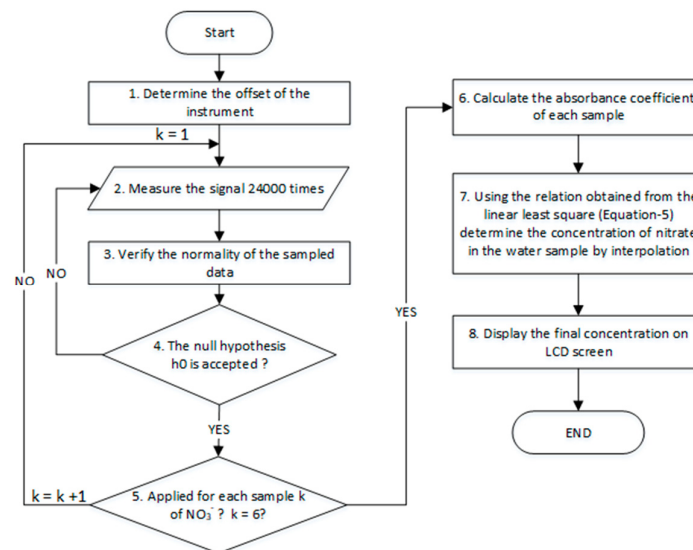


Figure 11. Flowchart of the implemented methodology used by NPMS.

2.8. Chemical Reagents and Fe²⁺ Samples

To evaluate the performance of the NPMS the results of the measured absorbance were compared towards the bench top laboratorial spectrophotometer Nicolet Evolution 300 by Thermo ELECTRON CORPORATION UV-Vis, controlled by VISIONpro PC CONTROL SOFTWARE. The Nicolet Evolution 300 is equipped with two quartz cells with 10 mm light path length and 300 mm height. One cell is loaded with the blank sample and the second with the standard solutions at concentrations of NO₃⁻. Table 2 present the characteristics of the spectrophotometer.

Table 2. Nicolet Evolution 300 Spectrophotometer characteristics.

Parameter	Value/Unity
Holographic grating	1200 lines/mm, blazed at 240 nm
Maximum resolution	0.5 nm
Range	190 to 1100 nm
Accuracy	± 0.20 nm (546.11 nm Hg emission line) ±30 nm (190 to 900 nm)
Repeatability peak separation of repetitive scanning of Hg line source	< 0.10 nm
Standard deviation of 10 measurements	<0.05 nm
Accuracy-instrument	1A: ± 0.004 A
	2A: ± 0.004 A
	3A: ± 0.006 A
Repeatability of the light intensity measurement	1A: ± 0.0025 A
Drift	<0.0005 Abs/hour at 500 nm, 2.0 nm SBW, 2 hr warm-up
Baseline flatness	± 0.0015 A (200 – 800 nm), 2.0 nm SBW, smoothed

To determine the NPMS performance, the standard curve, r-square coefficient, Pearson correlation and a statistical-F test, were assessed. The experiment started by measuring the spectra and determination the absorbance for NO₃⁻ samples at 302 nm using the reference instrument and then using the NPMS system. The flowchart shown in the (Figure 12) was implemented to determine the absorbance of NO₃⁻ in the prepared samples. In order to maintain the stability of the measurements, the cell was kept in the support and the water samples exchanged using a syringe.

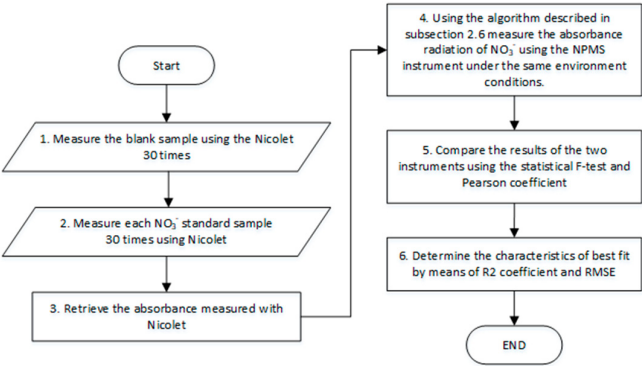


Figure 12. Flowchart of the implemented methodology to compare both instruments.

3. Results and Discussion

3.1. Sensitivity Analysis

The properties of the linear regression which includes the coefficient of determination, the coefficients of linear least square equation and the root-mean-square error (RMSE) are presented in the (Figure 13). The relation between the variances of the two instruments were determined by means of the statistic F-test. An uncertainty analysis with a confidence interval of 96% was performed to determine the instrument accuracy.

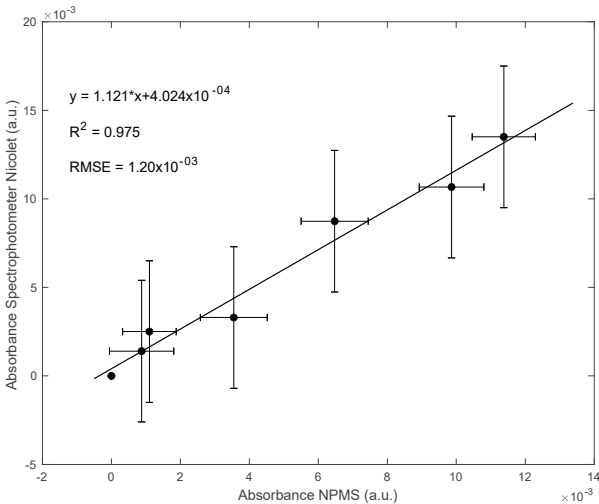


Figure 13. Absorbance retrieved with the NPMS towards the absorbance measured with the Spectrophotometer Nicolet.

The linear function presented a slope of 1.121 and an intercept of 4.02×10^{-4} , indicating a strong relation between both devices regarding the measured absorbances. This is also proven by the determination of R^2 , which denotes a value of 0.975. Overall, is observed an absorbance overestimation of the NPMS by 2.45% compared with Spectrophotometer Nicolet Evolution 300. The RMSE denotes a value of 1.24×10^{-3} , and the Pearson coefficient is 0.987 which indicates a strong positive linear relation. The result of the F-test presents an equality in the variance of both instruments, for a 5% significance level. In the Table 3 are presented the absorbance measurements for the NO_3^- standards as well as the F-test, variance and the critical values.

Table 3. Results for the measurement standards obtained with the NPMS and Nicolet Evolution 300.

Sample (mg NO_3^-/l)	Mean Abs.	Mean Abs.	Variance NPMS (mg NO_3^-/l)	Variance Nicolet (mg NO_3^-/l)	Critical Value
	NPMS	Nicolet			
5	0.0008	0.0014	2.1×10^{-07}	2.4×10^{-07}	1.10
10	0.0011	0.0025	1.5×10^{-07}	2.5×10^{-07}	1.65
25	0.0035	0.0033	2.3×10^{-07}	2.1×10^{-07}	0.89
50	0.0064	0.0087	2.3×10^{-07}	1.9×10^{-07}	0.82
75	0.0098	0.0106	2.1×10^{-07}	2.2×10^{-07}	1.01
100	0.0113	0.0135	2.0×10^{-07}	2.5×10^{-07}	1.19

3.2. Results for the NPMS's Calibration

The NPMS was calibrated using a series of standard solutions of NO_3^- , ranging from 5 mg NO_3^-/l to 100 mg NO_3^-/l . Once again, a very precise linear relation between the standard solutions and the

measured absorbance was found. The scatter plots in (Figure 14) shows the absorbance of the NO_3^- measured with the NPMS, towards the standard solutions, it also presents the calibration line obtained from the experimental data by means of linear least square fit, and which also allows to retrieve the unknown concentrations from the measured absorption. Furthermore, the R^2 coefficient and the value of the RMSE are reported to assess the fitting quality.

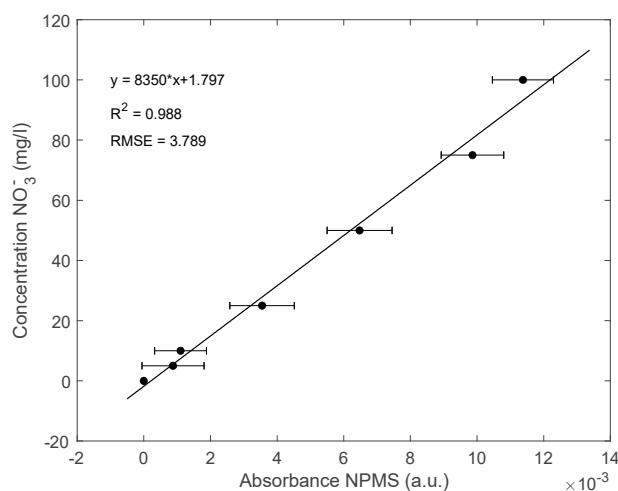


Figure 14. NPMS transfer function showing the integration of the recorded absorbance spectra of NO_3^- using the NPMS.

The abscissa presents the recorded absorbance, and the ordinate axis presents the concentration of the standard samples prepared in laboratory. The linear equation with the slope of 8350 and intercept of 1.797, was obtained and is the relation to use by the instrument to retrieve the NO_3^- concentration. The $R^2 = 0.988$ shows a good relation between the prepared NO_3^- samples and the absorbance, with a calculated RMSE = 3.789.

The calibration curve for the classical spectrophotometer Nicolet Evolution 300 at wavelength 302 nm is presented in (Figure 15). The linear equation with a slope of 7317 and an intercept of 4.06 to retrieve the NO_3^- concentration from the recorded absorption. The instrument also shows a $R^2 = 0.979$ and a RMSE = 5.15. Comparing the R^2 and the RMSE of the two instruments is possible to observe that the low-cost NPMS presents a better performance in retrieving the NO_3^- at wavelengths ranging between 295 and 315 nm than the spectrophotometer Nicolet due to a better RMSE and standard deviation.

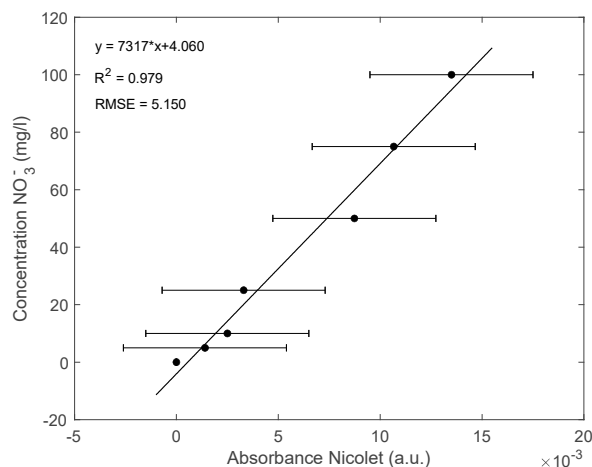


Figure 15. Transfer function of the classical spectrophotometer Nicolet at wavelength 302 nm.

4. Conclusions

The development, of a low-cost specialized NO_3^- portable measurement system (NPMS) have been successfully achieved for water samples. We have demonstrated the validity of using the 302 nm absorption peak for NO_3^- determination in aqueous solution. The use of a UV diode emitting radiation between 285 and 315 nm paired with a photodiode sensing from 240 to 360 nm, allows the measurement of NO_3^- absorption on the optimal spectra range without the interference of other chemical compounds or straylight. Thanks to this option, the cost of the device is significantly lower than it would be if the literature-recommended wavelength of 220 nm was used, due to the higher cost associated with the proper source for this spectral range.

The characterization of the LED performances shows a stable photon source characterized by a normal distribution and a standard deviation of ± 40 counts. The developed case allowed for the accommodation of all the instrument components in a small and robust footprint device that can be transported and deployed on the field for real time measurements. A comparison study between the NPMS and a classical spectrophotometer Nicolet was developed, and the results showed a good agreement between the two devices with high $R^2=0.975$. The F-test also presented a high correlation for the variances of the six NO_3^- standard samples as well as the Pearson correlation test with a value 0.987. Further work will be conducted to study the influence of the temperature over the system and to integrate a photon source with different wavelengths to allow multi-component detection and cross-interference corrections in particular organic matter at 275 nm wavelength and to apply the developed instrument to determine NO_3^- concentration in freshwater samples.

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